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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available.

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RESEARCH PAPER RP1513

Part of Journal of Research of the National Bureau of Standards, Volume 30, January 1943

MECHANICAL PROPERTIES OF CELLULOSE ACETATE AS RELATED TO MOLECULAR CHAIN LENGTH

By Arnold M. Sookne and Milton Harris [1]

ABSTRACT

The mechanical properties of films prepared from a series of fractions of cellulose acetate, varying widely in molecular chain length (*DP*), were determined. A fraction of *DP* 30 would not form a coherent film; fractions of higher *DP* showed a rapid improvement of mechanical properties with increase in *DP*, but above 150, further improvement was slight. A close correlation was found between the results of folding endurance and ultimate elongation measurements. These properties are more sensitive than tensile strength to changes in *DP* and heterogeneity with respect to *DP*. Investigation of the properties as a function of both weight-average and number-average *DP* indicated that at any given weight-average *DP*, the fractions are superior to the blends and furthermore, those blends which contain fractions of low *DP* are inferior to those which do not. In contrast, at any given number-average *DP* within the range studied, the properties of the fractions and all of the blends are approximately equal.

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I. INTRODUCTION

The mechanical properties of a cellulosic material are influenced by both the average molecular chain length (*DP*) [2] and the distribution of chain lengths of the molecules of which it is composed. There is

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

[2] By *DP* (degree of polymerization) is meant the average number of glucose residues per chain. For linear polymers, such as cellulose and its derivatives, *DP* is a measure of chain length. *DP* will henceforth be designated either DP_n, (number-average *DP*) or DP_w (weight-average *DP*). These are more specifically defined as follows:

$$DP_n = \frac{\Sigma n_i DP_i}{\Sigma n_i},$$

and

$$DP_w = \frac{\Sigma w_i DP_i}{\Sigma w_i},$$

where n_i is the number of molecules of DP, DP_i, and w_i is the total weight of that molecular species [1].

[3] Figures in brackets indicate the literature references at the end of this paper.

general agreement, at least for such linear high polymers, concerning the relationship between the *DP* and some of the mechanical properties of a series of relatively homogeneous fractions. Thus it has been shown that below a certain *DP*, characteristic for each material, no useful filaments or films can be formed. At slightly higher *DP*'s, there is a rapid improvement in the mechanical properties with increase of chain length, whereas at very high *DP*'s these properties are nearly independent of chain length [2, 3, 4].

No such agreement exists, however, concerning the relationship of chain length to mechanical properties when the materials are very heterogeneous. Several investigators have reported that a blended material gives films or filaments with mechanical properties superior to those prepared from a fraction of the same average DP_w's [5, 6, 7, 8]; others have found the blended materials to be inferior [3, 4, 7, 9] or approximately equal in properties [10]. Some of their results are summarized in table 1, which compares the properties of fractions and blends at corresponding DP_w's. In interpreting this table, it should be remembered that the results for films are not necessarily directly comparable with those for filaments, since the degree of orientation is probably considerably greater for the latter in most cases. In addition, the sensitivity of various mechanical properties to changes in homogeneity varies considerably. Unfortunately, most of the investigators have studied only the tensile strength, a property which has been shown to be relatively insensitive to changes in homogeneity [4].

In a previous publication [11], the preparation of a series of samples of fractionated cellulose acetate of widely different DP_w's was described. The present paper reports the results of studies of the effect of chain length and of heterogeneity with respect to chain length on a

TABLE 1.—*Homogeneity and mechanical properties of some high-polymeric materials*

Material	Mechanical properties investigated	Conclusions	Investigator	Reference
Cellulose acetate films	Tensile strength	Blends superior to fractions of corresponding *DP*'s.	Rocha	[5]
Cellulose acetate filaments.	do	do	Ohl	[6]
Do	do	Materials of low *DP* exert a harmful effect, and those of intermediate *DP* a beneficial effect on the tensile strengths of blends of the same average *DP*.	Mark	[7]
Cellulose nitrate films	Load-elongation curve.	In region of plastic flow of load-extension curve, blends require a higher load to produce a given elongation than do fractions of corresponding *DP*'s.	Medvedev	[8]
Do	Tensile strength, and ultimate elongation.	Little difference between fractions and blends.	Rogovin and Glazman.	[10]
Do	Tensile strength, ultimate elongation, and folding endurance.	Folding endurances of blends inferior to those of fractions of corresponding *DP*'s. Tensile strengths and ultimate elongations insensitive to changes in heterogeneity.	Spurlin	[1]
Viscose filaments	Numerous measures of strength and flexibility.	Material of low *DP*'s exerts a disproportionate harmful influence on the mechanical properties of blends.	Schieber	[9]
Vinyl chloride-acetate copolymer plastic.	do	Blend inferior in fatigue resistance and approximately equal in strength to fraction of corresponding *DP*.	Douglas and Stoops.	[3]

number of the mechanical properties of films prepared from these materials and their blends.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

The cellulose acetate fractions have been described in a previous publication [11]. They varied in DP_w, as determined viscometrically, from 30 to 380.

2. METHODS

(a) PREPARATION OF FILMS

Films 0.0025 to 0.0035 in. thick were prepared as follows: An acetate sample was shaken with a quantity of acetone, sufficient to give a solution with a viscosity of about 400 centipoises, until a homogeneous solution was obtained. The solution was poured onto a glass plate, and spread with a doctor blade, which was held at a predetermined distance above the plate by means of runners. The plate was then placed in a carefully leveled rack. The above operations were performed in a cold room which was maintained at a temperature of approximately 10° C to decrease the rate of evaporation of the acetone. When the film was dry, it was wetted with water, removed from the plate, and then soaked in distilled water at 50° C for 3 hours to remove residual solvent. Films prepared by this method were uniform in thickness to ± 0.0003 in.

(b) ESTIMATION OF RELATIVE WEIGHT-AVERAGE CHAIN LENGTH

The DP_w's of the blends were estimated viscometrically in the same manner as was previously used for the fractions [11]. The specific viscosities of dilute solutions of the blends in Methyl Cellosolve (ethylene glycol monomethyl ether) were measured at 25° and 60° C, and Staudinger's relationship [12] was used to calculate the DP's. The DP's reported later are the means of the values obtained at the two temperatures. Because of the limitations of the method of determining them [13], the DP values should be considered as relative values.

(c) MEASUREMENT OF MECHANICAL PROPERTIES OF FILMS

All the measurements of the mechanical properties of the films were made in an atmosphere having a relative humidity of 65 percent and a temperature of 21.1° C. Films approximately 0.003 in. thick were used for all of the tests. The actual thickness of each test sample was measured with a dial gage (graduated in ten-thousandths of an inch and with a foot pressure of 4 lb/in^2.

The tensile strengths and ultimate elongations of the samples were measured on a "constant-rate-of-elongation" Schopper tensile tester equipped with a recording chart. Samples 0.25 in. wide were used. The distance between the jaws was 3 in., and the rate of separation of the heads was 12 in. per minute when the machine was running free. The minimum thickness of each strip was used in calculating the tensile strengths. At least 10 measurements were made on each fraction and blend. The probable error of the mean for a set of measurements was approximately 3 percent for the tensile strengths and 10 percent for the ultimate elongations.

The folding endurances of the samples were measured by means of an MIT fold tester [14], with a tension of 1.5 kg. Strips 1.50 cm wide were used. Since the folding endurance is fairly sensitive to the thickness of the test strip (thinner films having a higher folding endurance in this range of thickness), it was necessary to correct the results to a standard thickness (0.003 in.) of test strip. This was done by applying small empirical correction factors, which were determined by measuring the folding endurances of strips of the same material but of different thicknesses. The correction factors were determined for several blends of fractions as well as for two commercial cellulose acetates, and were found to agree within 4 percent for a given thickness. About 15 strips were used for the measurement of the folding endurance of each fraction and blend. The probable error of the mean was approximately 8 percent.

Folding-endurance measurements were made both in the direction in which the doctor blade was moved in spreading, and at right angles to this direction. No significant difference was found in the properties in these two directions. This result indicates that, as far as the mechanical properties are concerned, the films do not have "machine" and "cross" directions.

The bursting strengths of the films prepared from the fractions were measured on a Mullen tester [15]. Ten bursts were made for each sample, and the results were corrected to a film thickness of 0.003 in.

III. RESULTS

1. MECHANICAL PROPERTIES OF THE FRACTIONS

The variation of the tensile and bursting strengths of the fractions with DP_w is shown in figure 1. As would be expected, there is a close correspondence between the two properties [15]. The general shape of the curve for the tensile strengths agrees well with the results obtained by other investigators [2, 3], although it is apparent that the strength is by no means independent of chain length in the range of *DP*'s covered by these materials. The material of *DP* 30 would not form a coherent film, and was therefore assigned a strength of zero.

In addition to the above measures of strength, impact-strength measurements were made on thin, narrow strips of the fractions.[4] The shape of the curve obtained by plotting impact strength against DP_w was closely similar to that for the bursting and tensile strengths. It is of interest to note that for all three of the strength tests described above, the starting material (designated by tagged circles in fig. 1) appears to be only slightly, if at all, inferior to a fraction of corresponding DP_w.

The ultimate elongations and folding endurances of the fractions are shown in figure 2. The results indicate a close relationship between these two quantities, and as will be shown later (section III–2), a similar correspondence was found for the blends. Both of these mechanical properties appear to be independent of chain length above a DP_w of approximately 150. The original material does not appear to differ significantly from a fraction of corresponding DP_w.

The first fraction obtained in the fractional precipitation procedure was characterized by its haziness and high ash content. Because it

[4] We are indebted to F. D. Pilgrim and W. O. Kearse of the Tennessee Eastman Corporation for making the impact-strength measurements.

was not completely soluble in acetone or Methyl Cellosolve, no estimate of its DP_w was obtained, and the data for its mechanical properties are therefore not included in figures 1 and 2. This material had a tensile strength of 1,000 kg/cm^2, a folding endurance of 86, and an ultimate elongation of 18 percent. These mechanical properties are similar to those of the fractions of high DP_w.

It should be noted that at low DP_w's, the folding endurance is much

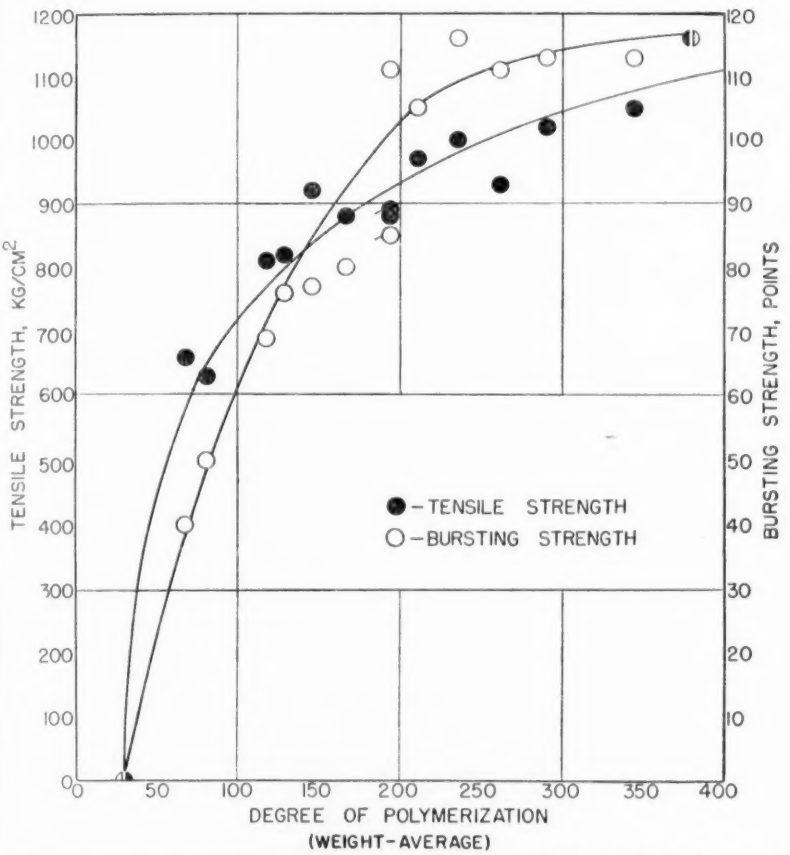

FIGURE 1.—*Tensile and bursting strengths of cellulose acetate fractions as a function of the viscometrically estimated DP.*

The starting material is designated by tagged circles.

more sensitive to variation in chain length than is the tensile strength. The ratio of the highest folding endurance to the lowest (with the exception of the fraction that will not form a film) is about 5:1; the corresponding ratio for the tensile strengths is less than 2:1.

A number of other mechanical properties [5] of the fractions were measured in addition to those described above. They are referred

[5] Measurements have been made of the flow characteristics (elongation as a function of time at constant load) of several of the fractions and the starting material. These results will be presented elsewhere, together with some results of load-elongation measurements on these materials [16].

to only briefly, since they show little variation with chain length. Films prepared from fractions of *DP*'s 67 and 380 were found to have moduli of rigidity which did not differ significantly. The flexural resiliencies, as measured with the Schiefer Flexometer [17], of these

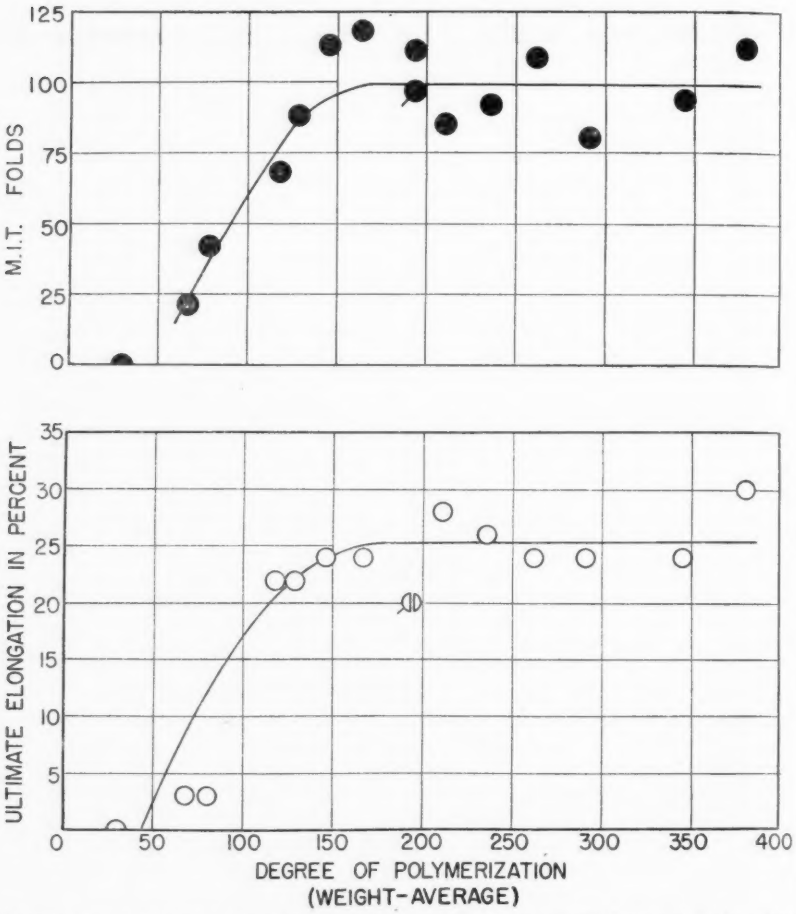

FIGURE 2.—*Ultimate elongations and folding endurances of cellulose acetate fractions as a function of the viscometrically estimated DP.*

The starting material is designated by tagged circles.

two fractions and of the starting material were found to agree within the experimental error.

2. MECHANICAL PROPERTIES OF BLENDS OF THE FRACTIONS

In order to study the effect of heterogeneity with respect to molecular chain length on the mechanical properties, a comparison of these properties for blends of different composition was made. The results are given in table 2 and shown graphically in figures 3 to 7.

TABLE 2.—*Properties of blends of cellulose acetate fractions*

Designation	Composition	Weight percentage of lower *DP*	Weight-average *DP* (calc.)	Weight-average *DP* (obs.)	Number-average *DP* (calc.)	Folding endurance	Tensile strength	Ultimate elongation
						Folds	*kg/cm²*	*Percent*
1 [a]	380+30	0	380	380	380	112	1,160	30
A	380+30	5	363	360	240	90	1,140	26
B	380+30	25	293	281	97	81	900	21
C	380+30	51	200	180	55	34	690	10
D	380+30	75	118	106	39	10	600	2
E	380+30	95	48	47	31	0	0	0
15 [a]	380+30	100	30	30	30	0	0	0
F	380+81	5	365	369	321	114	1,010	19
G	380+81	25	305	294	197	134	1,050	24
H	380+81	60	200	169	118	67	730	9
I	380+81	80	141	134	96	75	780	12
J	380+81	95	96	99	85	58	730	8
13 [a]	380+81	100	81	81	81	42	630	3
K	380+167	5	369	370	358	122	1,180	31
L	380+167	45	284	279	241	130	1,009	25
M	380+167	84	200	198	184	108	820	18
N	380+167	95	178	179	172	132	960	25
O	380+167	100	167	167	167	117	880	24
P	380+68	58	200	183	104	67	780	10
Q	380+129	59	255	247	193	103	1,020	25
R	380+129	72	200	196	158	125	780	17
S	291+81	43	200	195	138	74	940	24

[a] The properties of the fractions of *DP*'s 30, 81, 167, and 380 have been included for comparison. The fractions are numbered to correspond with their designations in a previous paper [11].

Figure 3 shows the tensile strengths of the blends plotted against DP_w. The curves for the three series of blends (DP_w's 380+30, 380+81, and 380+167) have been represented by solid lines as a matter of convenience, although the data are such that these curves are somewhat ambiguous. The dotted line, which is traced from figure 1, is the curve for the fractions. The results appear to indicate a small but measurable harmful effect of the shorter chains on the tensile strength, since the results for the blends fall below the dotted line in general, especially for those blends which contain the fraction of DP_w 30.

A similar but much larger effect is shown by measurements of the folding endurance and ultimate elongation (fig. 4). The curves for the series of blends 380+81 and 380+30 are markedly lower than the curves for the fractions (dotted lines, traced from fig. 2). The line for the folding endurances of the series 380+167 is, however, somewhat higher than the corresponding curve for the fractions. While there is a possibility that this may represent a slight superiority of these blends over the fractions, this does not appear too likely, since this effect is not shown by the results of the ultimate elongation measurements.

The effect of the shorter chains on the mechanical properties of blends of different composition, but all of DP_w 200 is shown in figure 5. The values of the mechanical properties for the blends of the pairs 380+30, 380+81, and 380+167 were interpolated from the smooth curves of figures 3 and 4, and the other points represent the values for blends *P* and *Q* of table 2. The graphs clearly demonstrate that the effect of heterogeneity is greater on the folding endurance and ultimate elongation than it is on the tensile strength.

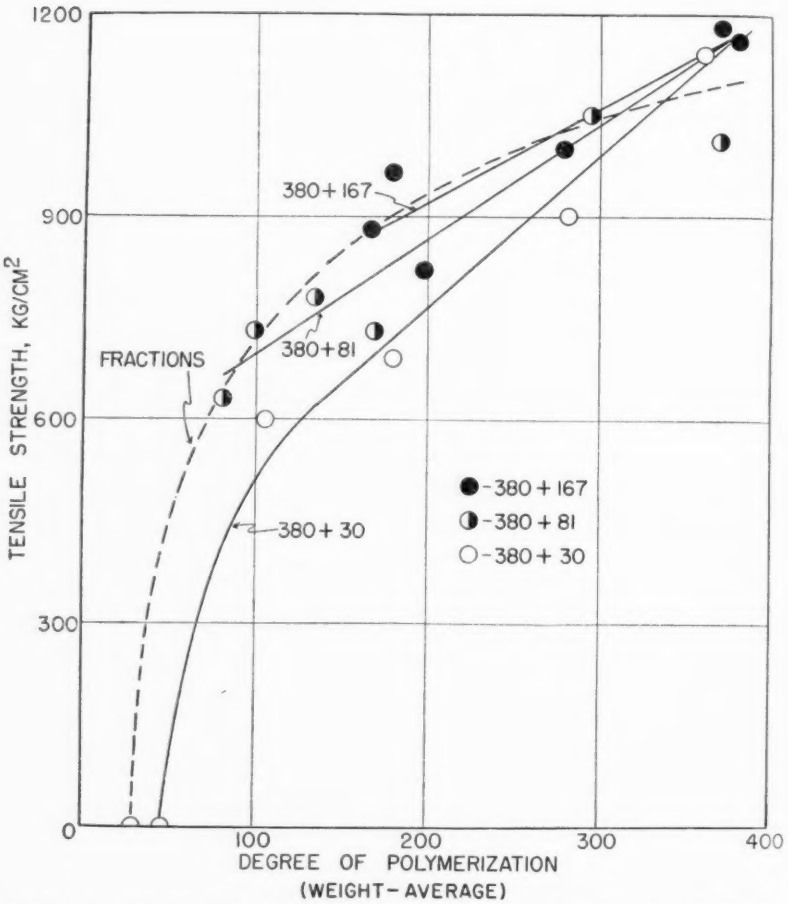

FIGURE 3.—*Tensile strengths of blends of cellulose acetate fractions as a function of the viscometrically estimated (weight-average) DP.*

The dotted line is the curve for the fractions, traced from figure 1. The tagged circle is common to all three series of blends.

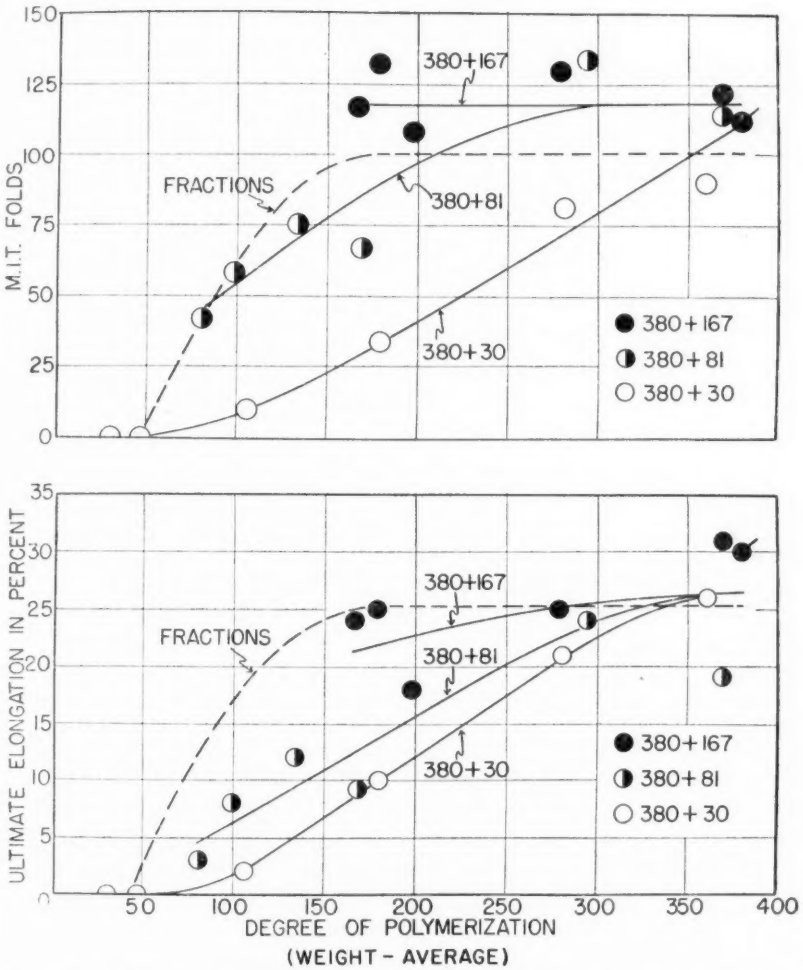

FIGURE 4.—*Ultimate elongations and folding endurances of blends of cellulose acetate fractions as functions of the viscometrically estimated DP.*

The dotted lines are the respective curves for the fractions, traced from figure 2. The tagged circles are common to all three series of blends.

The data presented above indicate that at a given DP_w, the materials of shorter chain length exert a harmful effect on the mechanical properties of blends. It is of particular interest to plot the data on the basis of the DP_n's of the fractions and blends as well. This requires the estimation of the DP by other means (such as osmotic pressure measurements) but since such data were not available,[6]

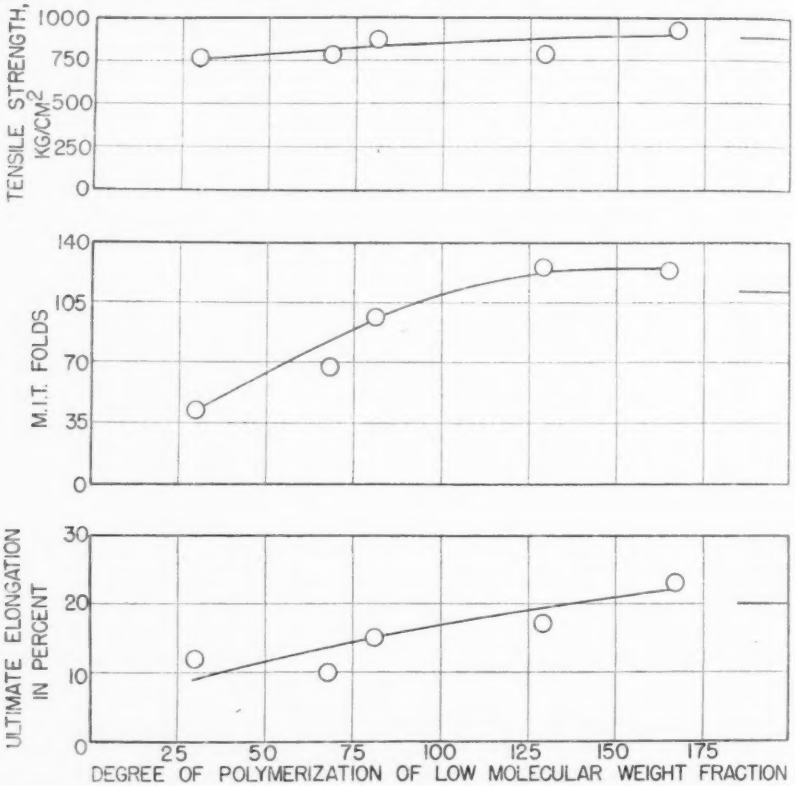

FIGURE 5.—*Mechanical properties of a series of blends, all of weight-average DP 200.*

The blends are composed of fractions of *DP*'s 380 and *X*. The mechanical properties are plotted as functions of *X*, the viscometrically estimated *DP* of the component of shorter chain length. The mechanical properties of a fraction of *DP* 194 are represented by the bars at the right side of the graphs.

recourse was had to calculated values.[7] These are given in column 6 of table 2.

[6] Measurements in progress.

[7] The values of DP_n for the blends can be calculated from the formula

$$DP_n=\frac{100}{\frac{f_1r_1}{DP_{w_1}}+\frac{f_2r_2}{DP_{w_2}}},$$

where DP_n is the number-average *DP* of the blend, f_1 and f_2 are the weight percentages in the blend of the fractions of DP_{w_1} and DP_{w_2}, respectively, $r_1=DP_{w_1}/DP_{n_1}$ and $r_2=DP_{w_2}/DP_{n_2}$. Since the fractionation process produces fractions that are relatively homogeneous, r_1 may be taken equal to r_2. The formula given above then reduces to the following:

$$DP_n=\frac{100}{r_1\left(\frac{f_1}{DP_{w_1}}+\frac{f_2}{DP_{w_2}}\right)}.$$

The figures given in column 6 of table 2 were calculated from this formula, with a value of unity assigned to r_1. They therefore represent relative calculated values.

The mechanical properties of the blends are plotted against their calculated relative DP_n's in figures 6 and 7. The dotted lines are not drawn to fit the points but are the curves for the respective mechanical properties of the fractions, traced from figures 1 and 2. As shown in figure 6, all of the tensil-strength data for the blends, regardless of composition, are reasonably well represented by the curve for the fractions, although the data for the series of blends

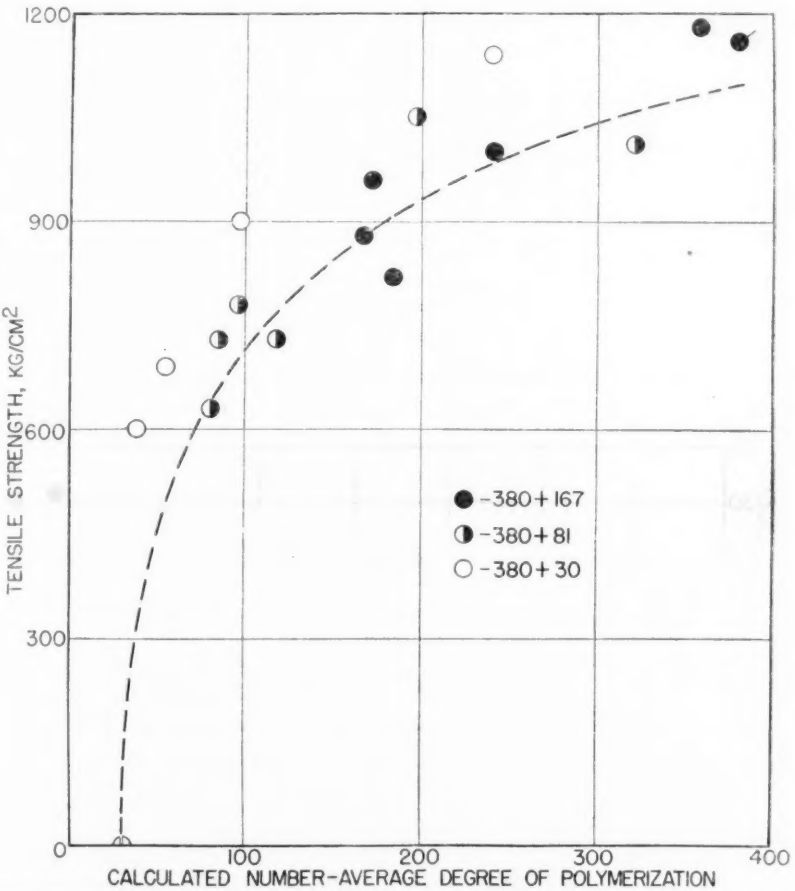

FIGURE 6.—*Tensile strengths of blends of cellulose acetate fractions as a function of the calculated number-average DP.*

The dotted line is the curve for the fractions, traced from figure 1. The tagged circle is common to all three series of blends.

380+30 (open circles, fig. 6) appear to be overcorrected by this method of calculation. Thus, in figure 6 the open circles fall above the dotted line in general, whereas in figure 3 (in which the tensile strengths are plotted against DP_w), they fall below it. A more critical test is provided by the folding-endurance data, since the differences caused by the admixture of material of short chain length

are apparently larger for this property. Figure 7 shows that the folding-endurance data for the blends are also reasonably well represented by the curve for the fractions (dotted line). The results for the ultimate elongations appear to parallel the results for the folding-endurance measurements. Figure 7 should be compared

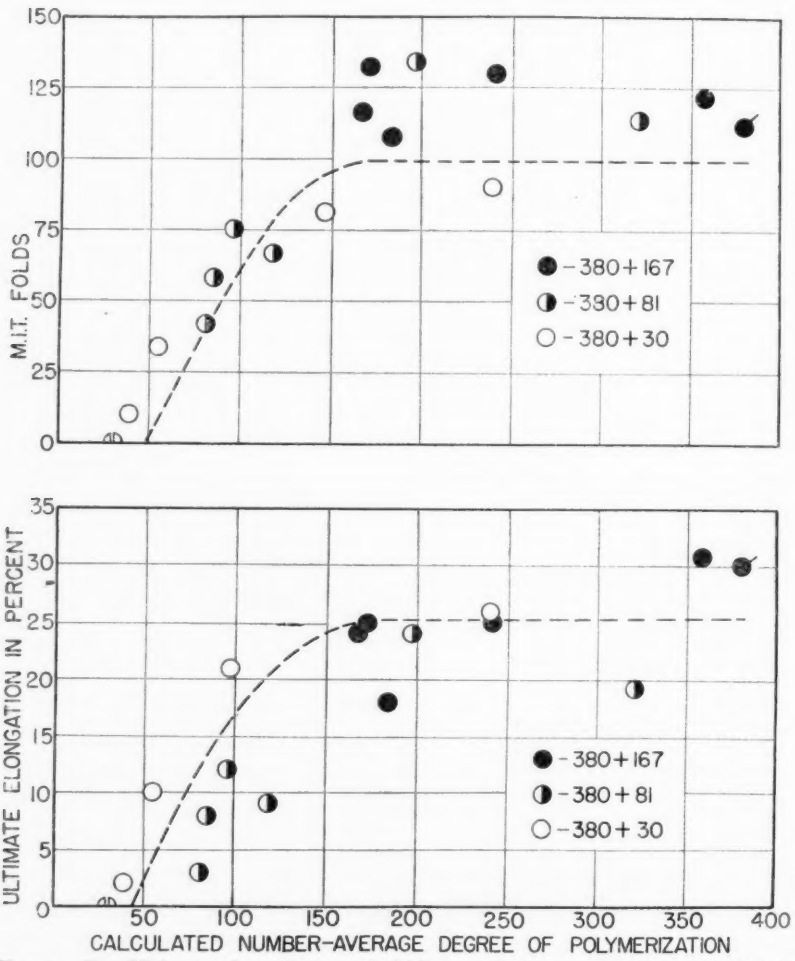

FIGURE 7.—*Ultimate elongations and folding endurances of blends of cellulose acetate fractions as functions of the calculated number-average DP.*

The dotted lines are the respective curves for the fractions, traced from figure 2. The tagged circle is common to all three series of blends.

with figure 4, in which the folding endurances and ultimate elongations are plotted against DP_w.

It is of interest to note that the results for the blends P, Q, R, and S (which have not been included in the curves) would also fall close to the dotted lines of figures 6 and 7.

IV. DISCUSSION

The data described above indicate that when the mechanical properties of the blends are plotted against their DP_w's, a harmful influence of the materials of shorter chain length (approximately DP_w 80 or less) can be observed. The magnitude of this influence is a function of the amount and *DP* of the shorter chains in a blend. On the other hand, the addition of a material of intermediate chain length to one of high *DP* does not appear to produce any marked beneficial or harmful effect. It may thus be said that under the conditions of these experiments, the mechanical properties are monotonic, but not single-valued functions of DP_w. On the other hand, when the mechanical properties of the blends are plotted against their calculated DP_n's, all of the data are reasonably well described by a single curve for each property. Since this curve approximates the curve for the fractions, it appears that the mechanical properties of the cellulose acetate films may be described as monotonic, single-valued functions of DP_n. In the absence of actual determinations of DP_n, this must be regarded as only a tentative hypothesis. It is interesting to note, however, that this hypothesis is qualitatively consistent with the concept that a sample ruptures in the tensile- or folding-endurance tester when a sufficient number of chain ends exist close together in the test strip [18]. This follows, since the number of chain ends in a cross-sectional element of the sample is inversely proportional to DP_n. It should be further noted, however, that the range of *DP*'s covered by these experiments is not very large. It is quite likely that the empirical generalization advanced above would not describe the results adequately if materials of very high and very low *DP*'s were blended. The results suggest, however, that for many industrial products, and particularly where materials of high and low *DP*'s are blended, considerable advantage would attach to the determination of DP_n, since this quantity appears to be more closely related to the mechanical properties than DP_w.

The results described above are consistent with those obtained by a number of other investigators [3, 4, 9]. Since the results of Spurlin [4] on the mechanical properties of nitrate films were obtained under experimental conditions rather similar to those described above, they are of especial interest here. Spurlin found that at corresponding DP_w's, films prepared from fractions were superior in folding endurance to those prepared from straight-run commercial nitrocellulose, and that the latter were in turn superior to blends of the straight-run material. The differences in properties were attributed to differences in homogeneity, and in particular it was concluded that a reasonably smooth distribution curve is desirable in order to obtain good folding endurance. While this is an entirely reasonable deduction for the materials that were being investigated, the results of the present investigation indicate that consideration of the DP_n's of the blends and fractions might have led to a somewhat different interpretation of the results. Unfortunately, since Spurlin's blends were not prepared from fractions, it is impossible to calculate even approximate relative values of the DP_n's for his samples. The data are, however, at least qualitatively consistent with the hypothesis that has been presented above.

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PERFORATED COVER PLATES FOR STEEL COLUMNS: COMPRESSIVE PROPERTIES OF PLATES HAVING OVALOID PERFORATIONS AND A WIDTH-TO-THICKNESS RATIO OF 53

By Ambrose H. Stang and Martin Greenspan

ABSTRACT

Tests were made to determine the mechanical properties of perforated cover plates intended to be used as a substitute for lattice bars or batten plates in built-up box-type columns. Each test column was built up from one perforated plate and either two or four angles. Columns with unperforated plates were used as controls.

This paper gives the results of the tests on columns having plates of three different perforation spacings.

It was found that the perforated plates contributed to the strength, and especially to the stiffness, of the columns, and that the factor of stress concentration, due to the presence of the perforations, varied from 2 to 2.6 based on the gross area (1.7 to 2.1, based on the net area).

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I. INTRODUCTION

This paper is the fourth of a series dealing with the mechanical properties of perforated cover plates intended to be used as a substitute for lattice bars or batten plates in built-up box-type columns. An outline of the program, and results for plates having widths of 15 in. and of 25.5 in. have been given in previous Research Papers [1, 2, 3].[1]

In this paper are presented the test results for the *C3* series of plates. These plates were 20 in. wide by ⅜ in. thick, thus having a width-to-thickness ratio of 53. The perforated plates of this series had ovaloid perforations 9 in. wide. The net-to-gross cross-sectional area ratio was 0.55.

II. COVER-PLATE COLUMNS

1. GENERAL

The details of the *C3* plates and of the angles are shown in figure 1. The perforated *C3* plates were all of the same nominal dimensions as to length, width, thickness and number, size, and shape of perforation but differed with regard to perforation spacing (i. e., the distance between centers of adjacent perforations). The perforation spacing was 30 in. for the *C3A* plates, 42 in. for the *C3B* plates, and 54 in. for the *C3C* plates. The *C3D* plates had the same nominal dimensions as the perforated *C3* plates but had no perforations.

Each plate shown in figure 1 represents three like plates, designated *(0–1)*, *(2–3)*, and *(4–5)*, and the angle shown represents many like angles which were used interchangeably with the plates to form the columns of which the cross sections are shown in the figure. The angles used with the plates to form the columns are given in table 1.

TABLE 1. *Angles used for the C3 columns*

Column designation [1]	Angle designations
C3A (...) 2 angles	*C5A(2–3)*, *C5E(0–1)*.
C3A (...) 4 angles	*C5A(2–3)*, *C5E(0–1)*, *C5D(0–1)*, *C5L(2–3)*.
C3B (...) 2 angles	*C5D(0–1)*, *C5L(2–3)*.
C3B (...) 4 angles	*C5D(0–1)*, *C5L(2–3)*, *C5C(2–3)*, *C5L(4–5)*.
C3C (...) 2 angles	*C5C(2–3)*, *C5L (4–5)*.
C3C (...) 4 angles	*C5C(2–3)*, *C5L(4–5)*, *C5C(0–1)*, *C5D(4–5)*.
C3D (...) 2 angles	*C5A(0–1)*, *C5E(4–5)*.
C3D (...) 4 angles	*C5A(0–1)*, *C5E(4–5)*, *C5A(2–3)*, *C5E(0–1)*.

[1] The 3 columns represented by each of the above designations contained the same angles.

2. DIMENSIONS

The dimensions given in figure 1 are nominal. There were the usual commercial variations in the thicknesses and widths of the plates and angles. The variations in the dimensions of the perforations were considerably greater; for some plates the difference between the minimum and maximum perforation width was of the order of 0.1 in. The cross-sectional areas of the plates and angles, computed from the measured dimensions, are given in table 2.

[1] Figures in brackets indicate the literature references at the end of this paper.

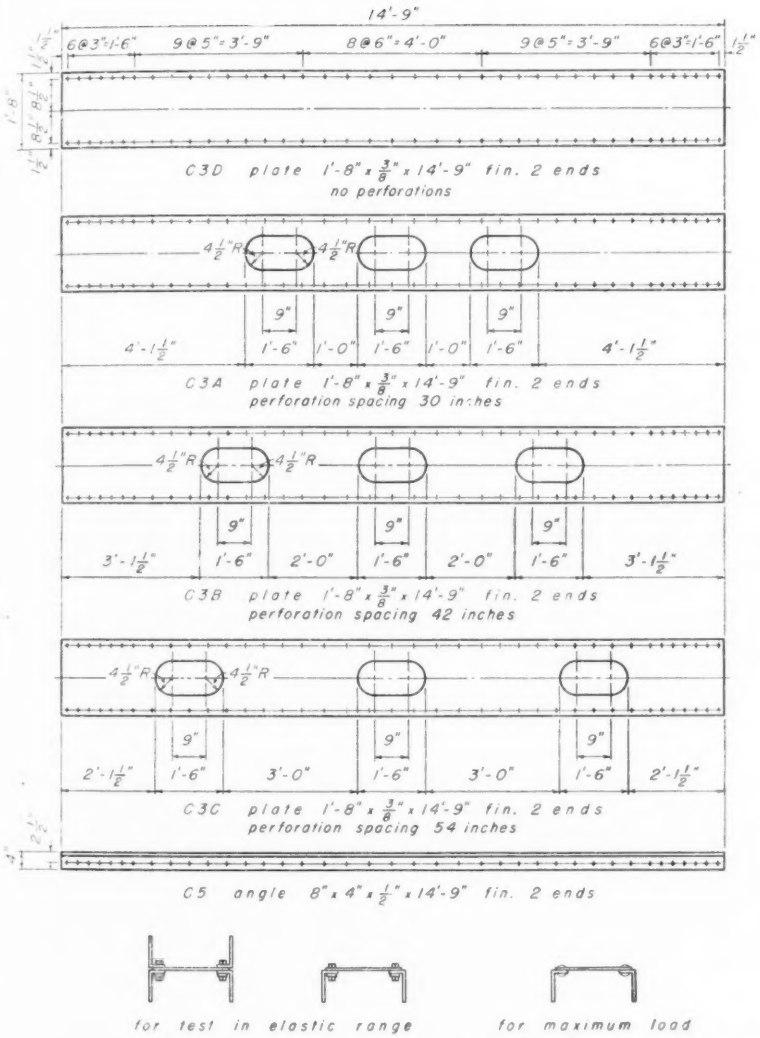

FIGURE 1.—*Plates and angles for the C3 columns*

TABLE 2.—*Cross-sectional areas of plates and angles for the C3 columns*

Plates			Angles	
Designation	Gross area	Net area	Designation	Area
	*in.*²	*in.*²		*in.*²
C3A(0-1)	7.64	4.25	*C5A(0-1)*	5.79
C3A(2-3)	7.60	4.22	*C5A(2-3)*	5.78
C3A(4-5)	7.56	4.18	*C5C(0-1)*	5.74
C3B(0-1)	7.75	4.31	*C5C(2-3)*	5.76
C3B(2-3)	7.65	4.25	*C5D(0-1)*	5.73
C3B(4-5)	7.65	4.25	*C5D(4-5)*	5.78
C3C(0-1)	7.72	4.28	*C5E(0-1)*	5.78
C3C(2-3)	7.60	4.21	*C5F(4-5)*	5.81
C3C(4-5)	7.50	4.13	*C5L(2-3)*	5.77
C3D(0-1)	7.67		*C5L(4-5)*	5.80
C3D(2-3)	7.62			
C3D(4-5)	7.57			

3. CONDITION OF ENDS

The plates and angles had been prepared with unusual care, so that the ends of the columns were reasonably flat. However, the ends were not flat in the sense that milled ends are flat. When the columns were stood on end on a flat steel plate, a definite tendency to teeter was observed.

III. PROCEDURE

1. COUPONS

Coupons representing the plate and angle material were cut in the direction of rolling and tested in tension. Young's modulus of elasticity, E; Poisson's ratio, μ; yield point, tensile strength, and elongation were determined.

A composite sample of the *C3* plate material and a composite sample of the angle material were analyzed for carbon, manganese, phosphorus, and sulfur.

2. COLUMNS

(a) ELASTIC RANGE

The shortening under load in the elastic range was determined for each column. The strains in the edge of the middle perforation were determined for each perforated-plate column. The strains in the surfaces of the plate were determined for the middle bay of one of each group of three like perforated-plate columns having four angles. The distribution of stress in the middle bay of each of these columns was calculated from the strain data and the values of the elastic constants obtained from the coupon tests.

(b) MAXIMUM LOAD

One two-angle column of each group of three like two-angle columns was subjected to the maximum-load test after the bolts had been replaced by rivets. Data to complete the stress-strain curves and data for the stress-deflection curves were taken.

IV. RESULTS

1. COUPONS

The results of the tensile tests of the coupons are given in table 3, and the chemical composition of the coupon material is given in table 4.

TABLE 3.—*Results of tensile tests of coupons*

Coupon designation	Thickness	Young's modulus of elasticity, E	Poisson's ratio, μ	Yield point	Tensile strength	Elongation in 8 in.
PLATE COUPONS						
	in.	*Kips/in.*²		*Kips/in.*²	*Kips/in.*²	%
C3A(1-2)	0.381	29,400	0.278	37.2	58.6	36.0
C3A(3-4)	.379	29,600	.282	38.0	59.0	30.5
C3B(1-2)	.385	29,500	.282	38.4	58.7	31.9
C3B(3-4)	.384	29,700	.282	37.1	58.7	31.9
C3C(1-2)	.383	29,500	.283	37.3	59.8	33.8
C3C(3-4)	.377	29,100	.278	37.3	59.7	35.5
C3D(1-2)	.382	29,400	.281	38.0	60.4	32.4
C3D(3-4)	.379	29,600	.276	38.6	60.5	32.7
ANGLE COUPONS						
C5A(1-2)	0.510	29,600	0.286	36.3	59.0	33.5
C5A(3-4)	.506	30,000	.290	35.6	58.1	33.5
C5C(1-2)	.508	29,400	.281	36.4	58.8	31.3
C5C(3-4)	.501	29,700	.285	34.8	58.3	33.0
C5D(1-2)	.500	29,800	.287	37.0	63.7	33.1
C5D(3-4)	.507	29,700	.288	36.9	64.5	33.0
C5E(1-2)	.508	29,700	.285	37.5	59.6	31.3
C5E(3-4)	.508	29,600	.281	36.0	59.1	33.1
C5L(1-2)	.503	29,500	.290	36.1	58.7	35.8
C5L(3-4)	.511	29,600	.286	36.6	59.1	34.6

TABLE 4.—*Chemical composition of coupon material*

Composite sample	Carbon	Manganese	Phosphorus	Sulfur
	%	%	%	%
Plates C3	0.17	0.54	0.008	0.033
Angles C5	.21	.56	.014	.03

2. COLUMNS

(a) MODULUS OF COLUMN AND EFFECTIVE AREA OF PLATE

The moduli, E', of the columns, and the effective-area factors, K, with respect to shortening under compressive load, for the plates, are given in table 5.[2]

[2] See pages 679 and 680 of reference [1].

TABLE 5.—*Moduli of columns, effective-area factors of plates, and maximum-stress ratios*

Plate designation	Number of angles	Based on gross area			Based on net area		
		Modulus, E'	Effective-area factor, K	Ratio Maximum stress / P/A	Modulus, E'	Effective-area factor, K	Ratio Maximum stress / P/A
		*Kips/in.*²			*Kips/in.*²		
C3A(0-1)	2	24,800	0.61		30,100	1.10	
C3A(2-3)	2	24,600	.60		29,900	1.07	
C3A(4-5)	2	24,700	.60		30,000	1.09	
Avg		24,700	0.60	−2.16	30,000	1.09	−1.78
C3A(0-1)	4	26,600	0.64		29,900	1.15	
C3A(2-3)	4	26,500	.62		29,800	1.11	
C3A(4-5)	4	26,600	.64		30,000	1.15	
Avg		26,600	0.63	−1.97	29,900	1.14	−1.75
C3B(0-1)	2	25,400	0.67		30,900	1.20	
C3B(2-3)	2	25,400	.67		30,900	1.20	
C3B(4-5)	2	25,600	.68		31,100	1.23	
Avg		25,500	0.67	−2.37	31,000	1.21	−1.95
C3B(0-1)	4	26,900	0.68		30,300	1.22	
C3B(2-3)	4	26,900	.67		30,200	1.21	
C3B(4-5)	4	26,900	.68		30,200	1.21	
Avg		26,900	0.68	−2.28	30,200	1.21	−2.03
C3C(0-1)	2	25,800	0.70		31,400	1.27	
C3C(2-3)	2	25,700	.69		31,200	1.24	
C3C(4-5)	2	25,800	.69		31,300	1.26	
Avg		25,800	0.69	−2.55	31,300	1.26	−2.10
C3C(0-1)	4	26,900	0.67		30,200	1.21	
C3C(2-3)	4	27,100	.70		30,400	1.26	
C3C(4-5)	4	27,100	.69		30,400	1.26	
Avg		27,000	0.69	−2.39	30,300	1.24	−2.13
C3D(0-1)	2	29,400			29,400		
C3D(2-3)	2	29,300			29,300		
C3D(4-5)	2	29,200			29,200		
Avg		29,300	1.00		29,300	1.00	
C3D(0-1)	4	29,300			29,300		
C3D(2-3)	4	29,300			29,300		
C3D(4-5)	4	29,200			29,200		
Avg		29,300	1.00		29,300	1.00	

(b) STRESSES

(1) *On the Edge of the Perforation.*—The distribution of stress on the edge of the middle perforation is indicated in figures 2, 3, and 4. Each curve represents the average result for three like columns having the same perforation spacing.

The vertical axis of the graph in each figure is a development of one quadrant of the edge of the perforation. The point B is the point of tangency of the circular and straight parts of the edge.

In the stress ratios, $\sigma_{u,s}/(P/A_n)$, A_n is the net area of the column, and σ_u and σ_s are the maximum and the minimum principal stresses, respectively. The stress ratios based on gross area, $\sigma_{us}/(P/A)$, may be obtained by multiplying $\sigma_{u,s}/(P/A_n)$ by 1.22 for the two-angle and 1.12 for the four-angle columns. The maximum stress ratios are given in table 5.

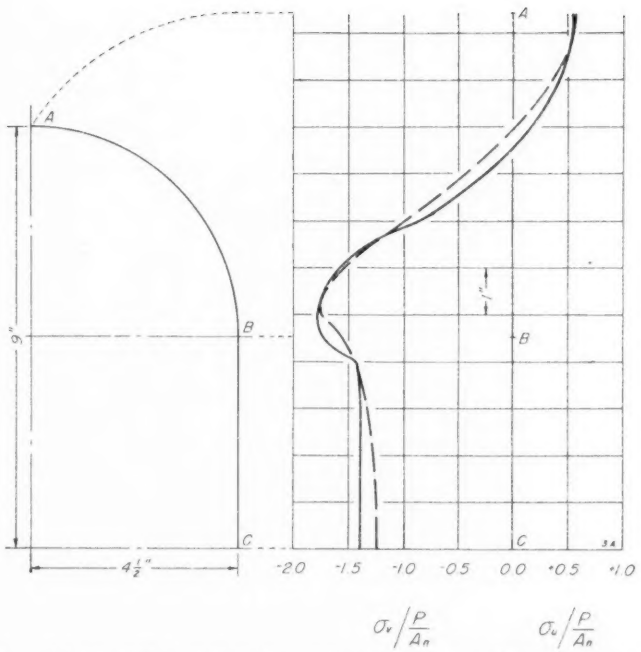

FIGURE 2.—*Columns C3A, perforation spacing 30 inches. Distribution of stress on the edge of the middle perforation.*

The solid line is for the two-angle, and the dashed line for the four-angle, column. Based on net area.

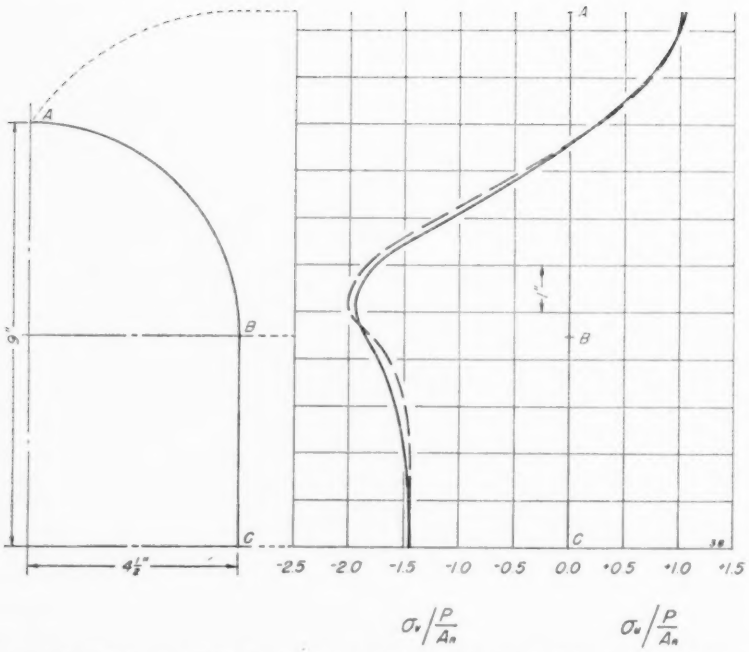

FIGURE 3.—*Columns C3B, perforation spacing 42 inches. Distribution of stress on the edge of the middle perforation.*

The solid line is for the two-angle, and the dashed line for the four-angle, column. Based on net area.

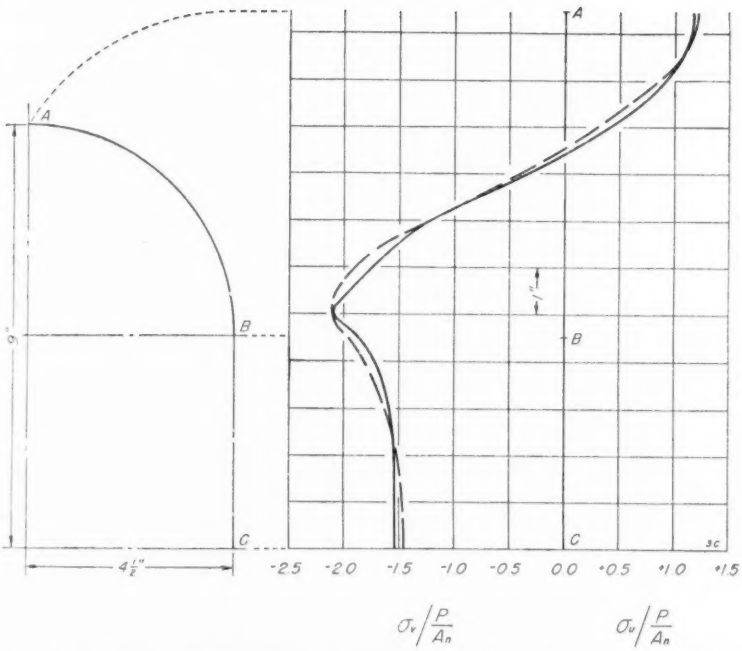

FIGURE 4.—*Columns C3C, perforation spacing 54 inches. Distribution of stress on the edge of the middle perforation.*

The solid line is for the two-angle, and the dashed line for the four-angle, column. Based on net area.

(2) *On the Surfaces of the Plate.*—The distributions of stress on the surfaces of the middle bay for the perforated-plate columns having four angles are indicated in figures 5 to 16, inclusive. The stress ratios shown in these figures are based on net area. The stress ratios based on gross area may be obtained by multiplying the given values by 1.12 for these four-angle columns.

The effect of the perforation on the stress distribution may be judged from the fact that for a solid plate (no perforation) the values everywhere of $\sigma_u/(P/A)$ are zero; of $\sigma_v/(P/A)$, -1; and of θ, 90 degrees.

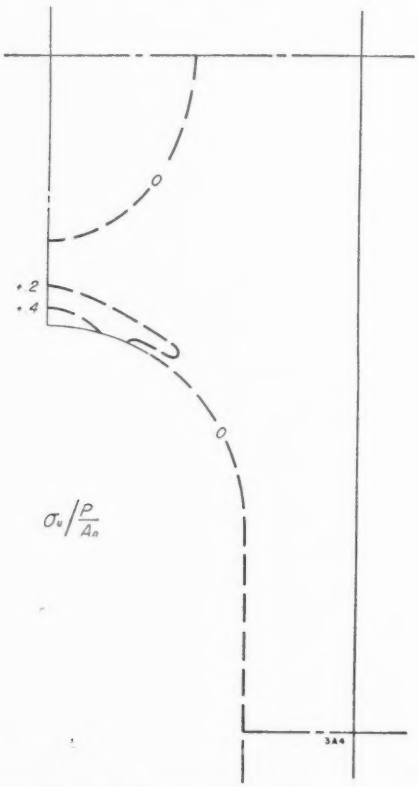

FIGURE 5.—*Column C3A(2–3) (four angles), perforation spacing 30 inches. Isogram of maximum principal stress.*

Based on net area.

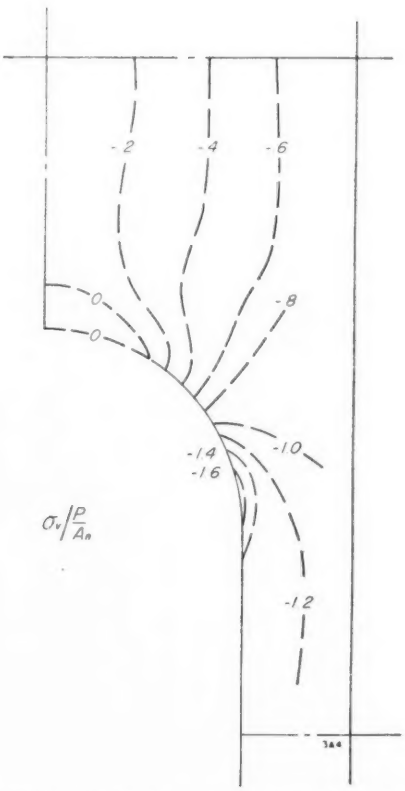

FIGURE 6.—*Column C3A(2–3) (four angles), perforation spacing 30 inches. Isogram of minimum principal stress.*

Based on net area.

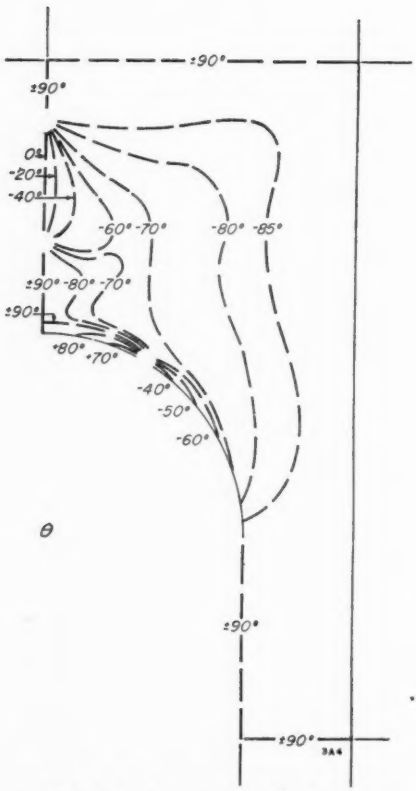

FIGURE 7.—*Column C3A(2–3) (four angles), perforation spacing 30 inches. Isoclinics.*

The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

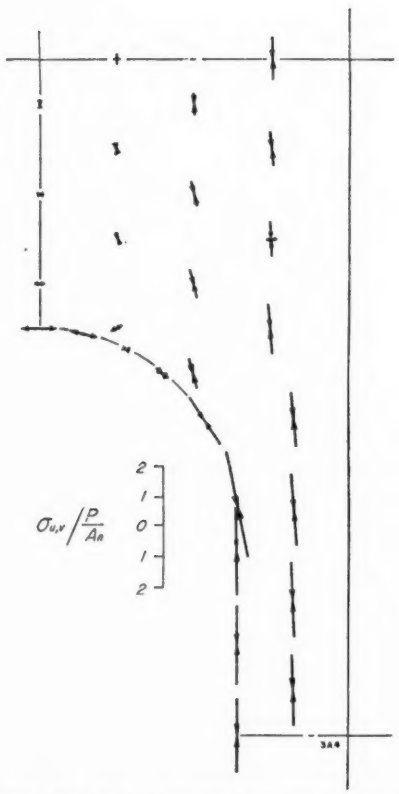

FIGURE 8.—*Column C3A(2–3) (four angles), perforation spacing 30 inches Magnitude and direction of the principal stresses.*

Based on net area.

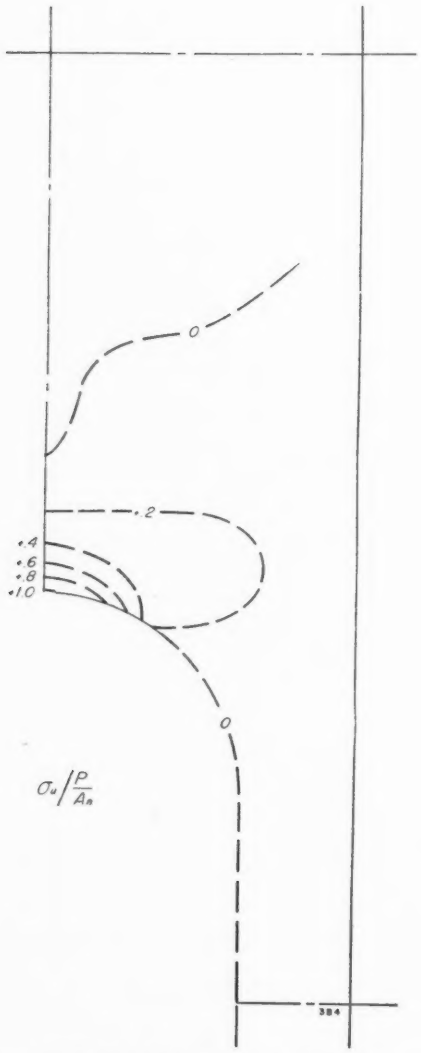

FIGURE 9.—*Column C3B(2–3) (four angles), perforation spacing 42 inches. Isogram of maximum principal stress.*

Based on net area.

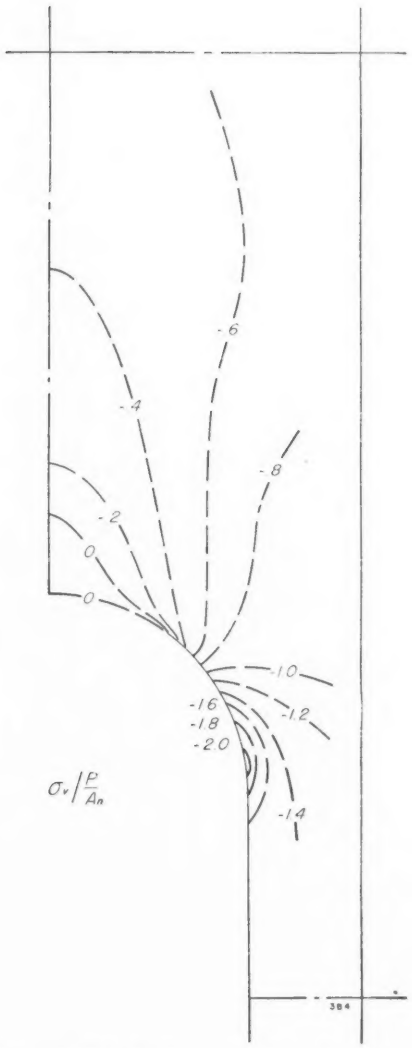

FIGURE 10.—*Column C3B(2–3) (four angles), perforation spacing 42 inches. Isogram of minimum principal stress.*

Based on net area.

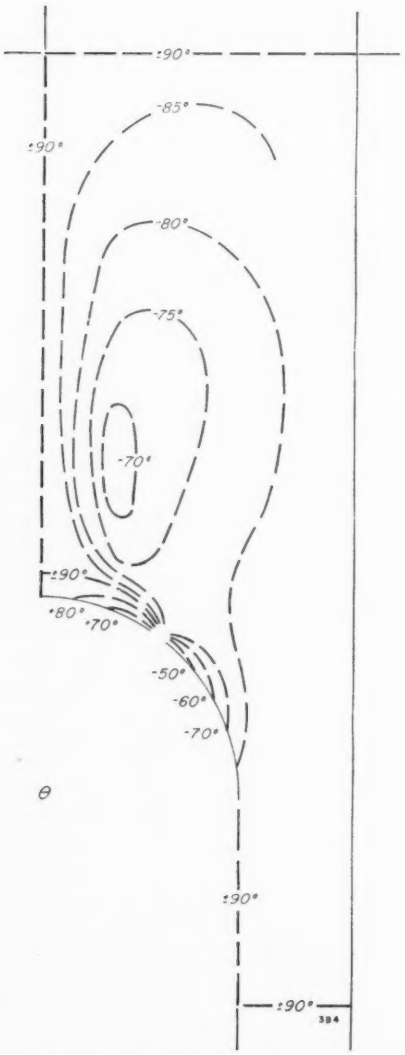

FIGURE 11.—*Column C3B(2–3) (four angles), perforation spacing 42 inches. Isoclinics.*

The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

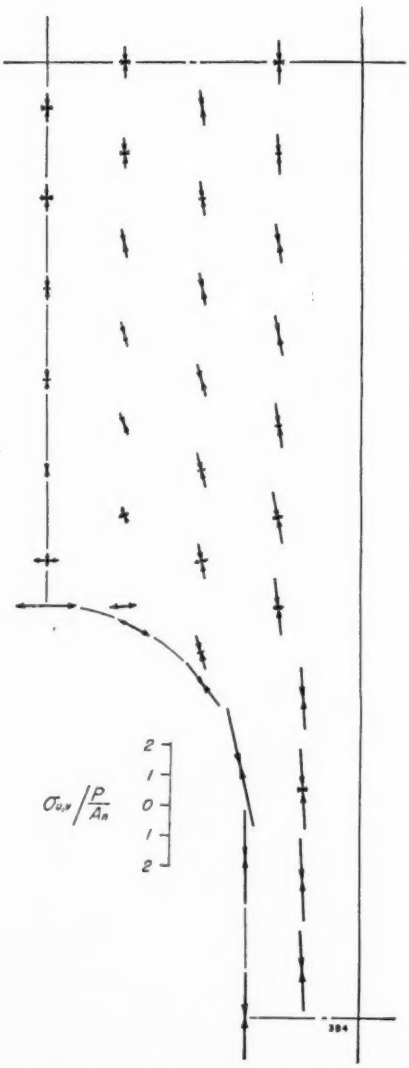

FIGURE 12.—*Column C3B(2–3) (four angles), perforation spacing 42 inches. Magnitude and direction of the principal stresses.*

Based on net area.

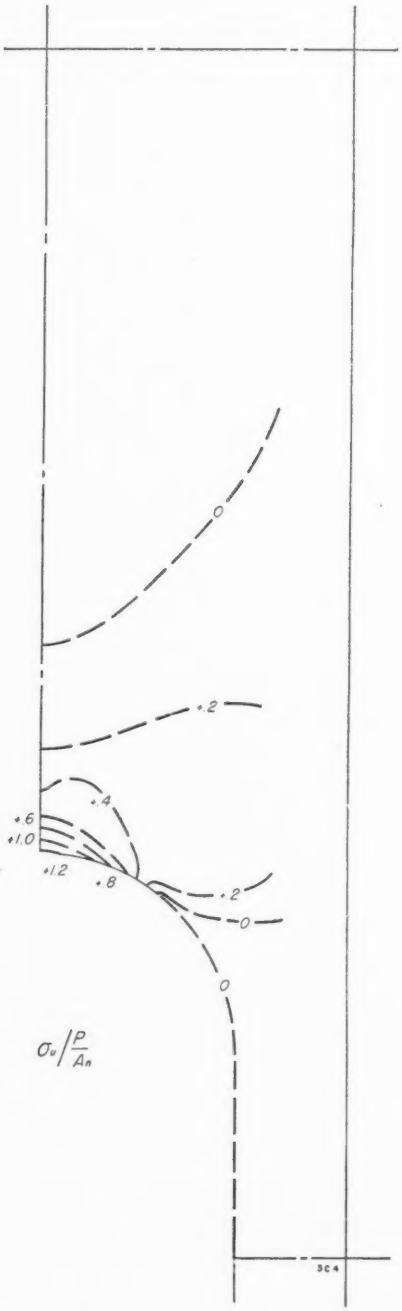

FIGURE 13.—*Column C3C(2–3) (four angles), perforation spacing 54 inches. Isogram of maximum principal stress.*

Based on net area.

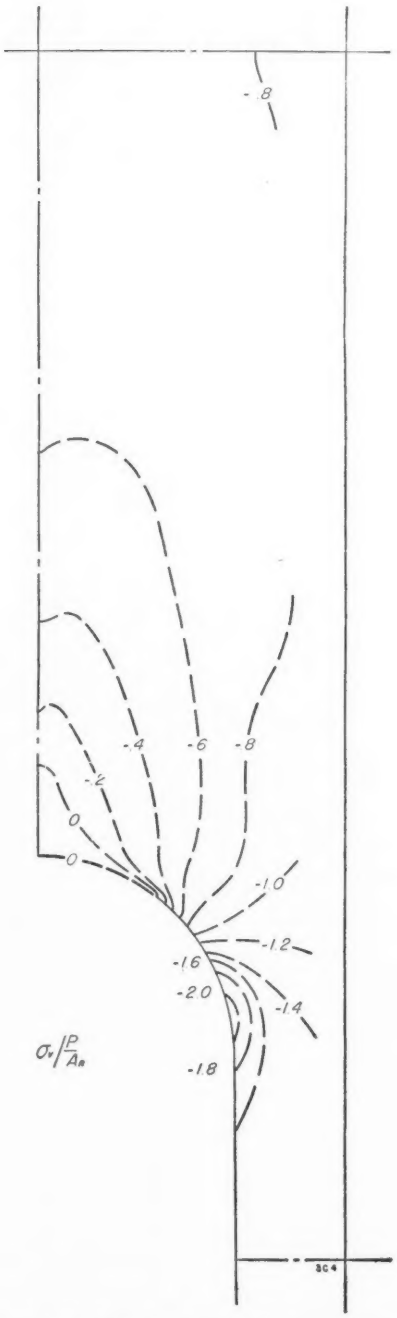

FIGURE 14.—*Column C3C(2–3) (four angles), perforation spacing 54 inches. Isogram of minimum principal stress.*

Based on net area.

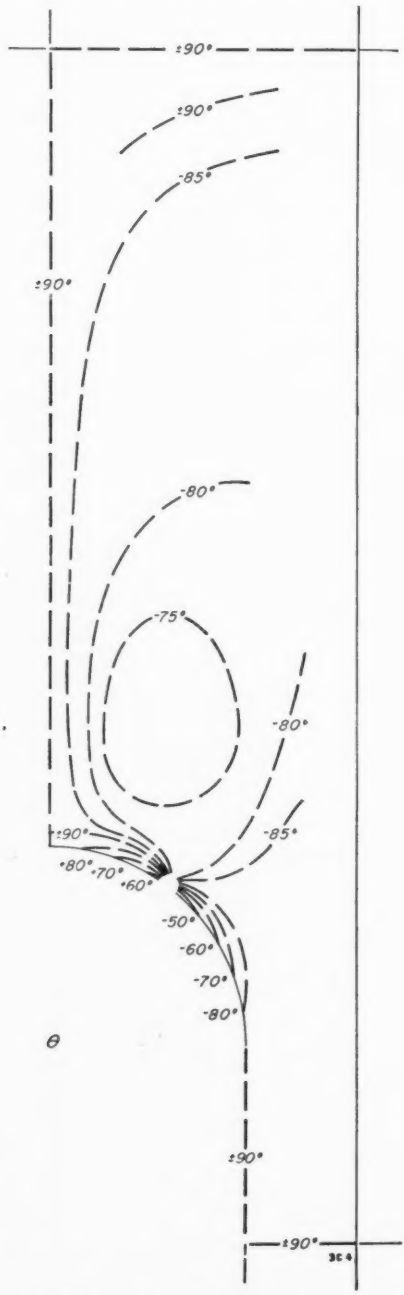

FIGURE 15.—*Column C3C(2–3) (four angles), perforation spacing 54 inches. Isoclinics.*

The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

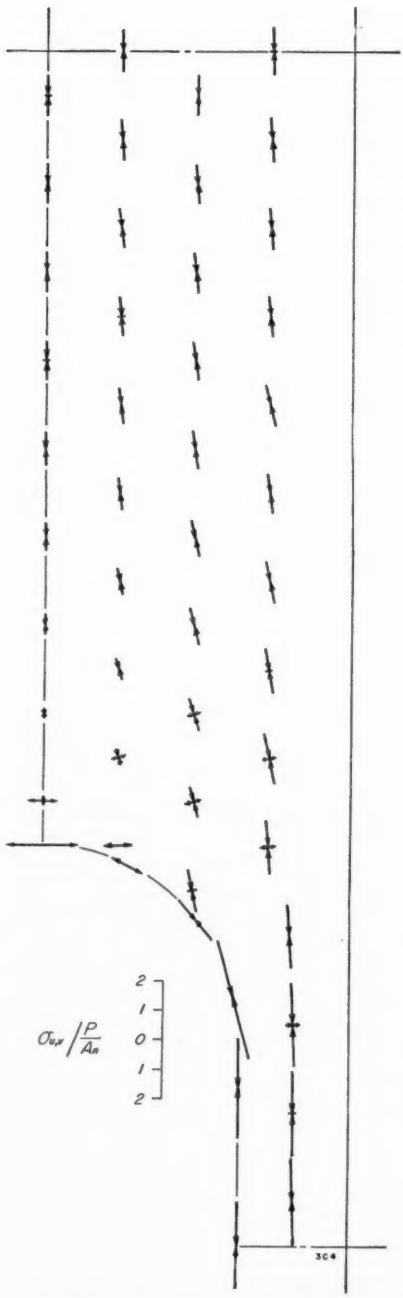

FIGURE 16.—*Column C3C(2–3) (four angles), perforation spacing 54 inches. Magnitude and direction of the principal stresses.*

Based on net area.

(c) MAXIMUM-LOAD TEST

(1) *Stress-Strain Graphs.*—The stress-strain graphs for the columns, based on net areas, are shown in figure 17.

The stresses on gross area may be obtained by multiplying the stresses on net area by 0.82.

(2) *Deflections.*—The stress-lateral-deflection graphs for the columns, based on net area, are shown in figure 18.

The stresses on gross area may be obtained by multiplying the stresses on net area by 0.82.

(3) *Maximum Load and Effective Area of Plate.*—The maximum loads for the columns, the maximum average stress on the gross area

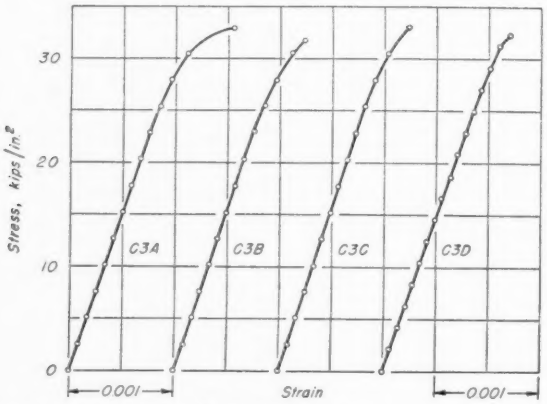

FIGURE 17.—*Columns C3–(two angles). Stress-strain graphs.*

Based on net area.

and on the net area, and the effective-area factors of the plates with respect to compressive strength, C, are given in table 6.[3]

TABLE 6.—*Maximum loads for columns and effective-area factors for plates*

Column designation	*C3A*	*C3B*	*C3C*	*C3D*
Perforation spacing, in	30	42	54	(a)
Area of angles, in.²	11.57	11.50	11.57	11.60
Gross area of plate, in.²	7.60	7.65	7.60	7.62
Net area of plate, in.²	4.22	4.25	4.21	7.62
Total area, gross, in.²	19.17	19.15	19.17	19.22
Total area, net, in.²	15.79	15.75	15.78	19.22
Maximum compressive load, kips	521	516	535	624
Compressive stress on gross area at failure, kips/in.²	27.2	26.9	27.9	32.5
Compressive stress on net area at failure, kips/in.²	33.0	32.8	33.9	32.5
Effective-area factor of plate with respect to compressive strength, C:				
Based on gross area	0.59	0.57	0.64	1.00
Based on net area	1.06	1.03	1.16	----
Slenderness ratio	----	----	----	71
Column efficiency, percent	----	----	----	87

[a] No perforation.

The perforated-plate columns *C3A*, *C3B*, and *C3C* failed by primary buckling away from the plate side of the column, as would be expected from the consideration that, in the neighborhood of a perfora-

[3] See page 685 of reference [1].

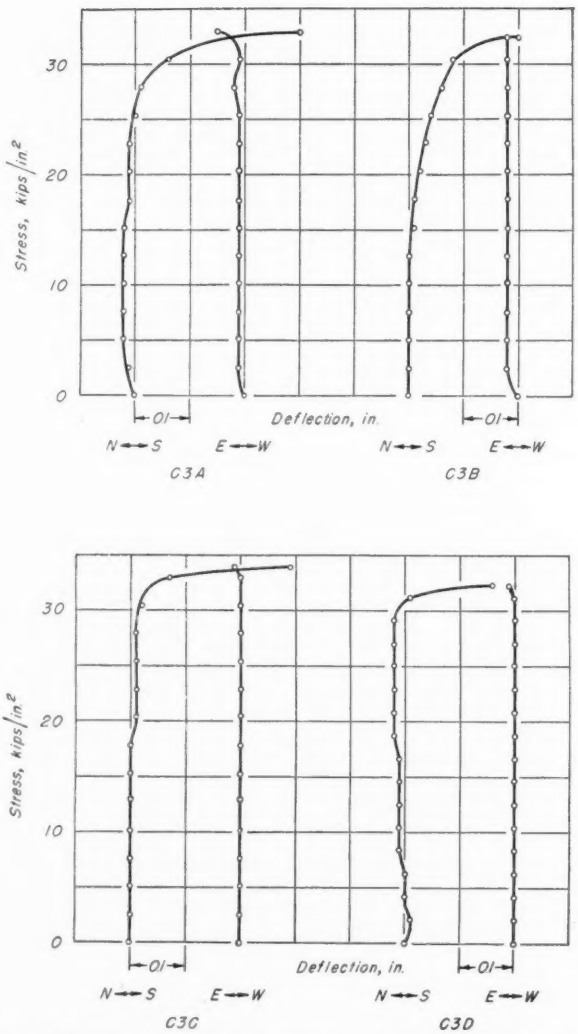

FIGURE 18.—*Columns C3–(two angles). Stress-deflection graphs.*

Based on net area. When the deflection is North, *N*, the bending stress is tensile on the plate side.

tion, the gravity axis of the column is displaced away from the plate side. Local buckling of the outstanding legs of the angles of the columns occurred near the ends of the column. The plates buckled near the middle perforation.

The unperforated-plate column *C3D* started to deflect toward the plate side, as would be expected from the double-modulus theory, but it failed by secondary buckling of the plate at about one-third the height of the column from the base. The column efficiency of 87 percent, given in table 6, is the ratio of the average stress at failure to the weighted average yield point of the material determined from the tensile tests of the coupons. This value of column efficiency is lower than would be expected for a column having a slenderness ratio of 71 tested with flat ends. This low-efficiency is due to the failure being at least partly by instability. The efficiency of column *C3D* is intermediate to the efficiencies of the two previously tested unperforated-plate columns, column *C2D* having a narrower cover plate and which failed largely as a whole, and column *C4D* having a wider cover plate and which failed largely by elastic instability.

The effective area factors, C, of the perforated plates with respect to compressive strength are of course greater than they would have been if the unperforated-plate column had failed at a higher stress owing to primary buckling. It may be noted that the compressive stresses on net area at failure are practically the same for the perforated-plate *C3* columns as for the previously tested perforated-plate *C2* and *C4* columns. Figure 19 shows the columns after test.

V. SUMMARY

1. MODULUS

The effectiveness of the perforated plates in resisting shortening under compressive load was determined by comparison of the modulus of a column containing the perforated plate with that of a similar column containing an unperforated plate. It was found that from 60 to 70 percent of the gross cross-sectional area of the plate, depending on the perforation spacing, was effective in resisting shortening under compressive load. The effective-area factors for the perforated plates were not consistently affected by variation in the number of angles with which they were tested.

2. STRESS DISTRIBUTION

The stress distribution was determined on the edge of the middle perforation of each perforated-plate column and on the middle bay of one of each group of three like columns having four angles. In every case the maximum stress was compressive and occurred on the edge of the perforation. The value of the maximum stress increased with increase of perforation spacing. For columns with the same perforation spacing, the maximum stress was higher for the two-angle than for the four-angle column for the same average stress on the gross area. This was not always true when the stresses were based on net area.

The maximum stress varied from 2 to 2.6 times the average stress on the gross area, or 1.7 to 2.1 times the average stress on the net area.

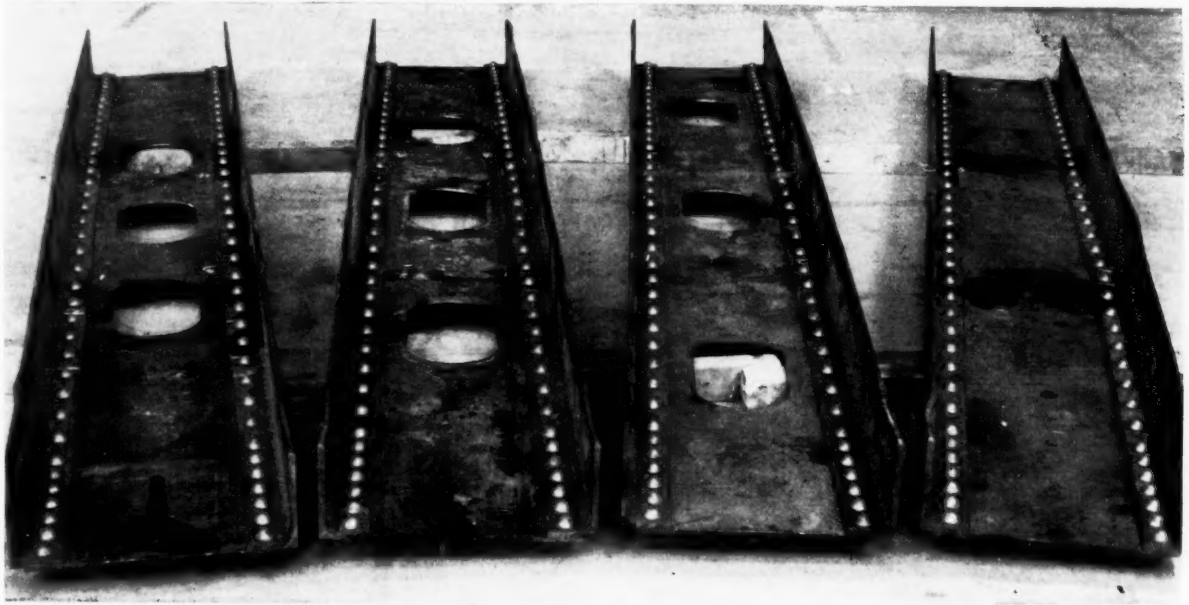

FIGURE 19.—*Columns C3–(two angles) after maximum load tests.*

From left to right the columns are *C3A, C3B, C3C, and C3D.*

3. STRENGTH

The effectiveness of the perforated plates with respect to strength was somewhat lower than with respect to resistance to shortening and was little affected by change of perforation spacing.

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WASHINGTON, October 5, 1942.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1515

Part of Journal of Research of the National Bureau of Standards, Volume 30, January 1943

AN IMPROVED ELECTRODE HOLDER FOR SPECTROGRAPHIC ANALYSIS*

By Bourdon F. Scribner and Charles H. Corliss

ABSTRACT

An electrode holder has been constructed for improving the speed and ease of operations in miscellaneous spectrographic testing. Advantages afforded by the new holder include: (1) application to a variety of electrode sizes and excitation conditions, (2) positive and precise adjustment and motion of the parts, (3) water-cooling of the electrode clamps, and (4) a housing for protection against light, fumes, and electric shock. The construction of the holder and its application to excitation problems with the high-voltage spark, the a-c arc, and the d-c arc are described.

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I. INTRODUCTION

Many of the parts of the spectrographic assembly have undergone marked improvement during recent years, but relatively little attention has been given to the design of the electrode holder, except for certain special applications. In addition to the common models based on the simple Gramont design, holders have been devised for a-c arc excitation of rods [1, 2] [1] or sheet metal [3], and for rapid change of spark electrode rods [4, 5] or metal plates [6]. A universal holder has been described [7] that provides a variety of electrode movements and adjustments.

For application in miscellaneous analyses, however, difficulty may be encountered when changes must be made quickly to handle electrodes of different sizes and shapes and from one extreme of excitation conditions to another. To meet these demands, a holder has been constructed incorporating the following features: (1) ease and speed of operation over the varied conditions encountered, (2) precise adjustment and motion of parts to prevent errors caused by poor alinement

*Presented at the Tenth Annual Conference on Applied Spectroscopy (at MIT) on July 22, 1942.

[1] Figures in brackets indicate the literature references at the end of this paper.

of electrodes, (3) water-cooling of electrode clamps to remove excessive heat, thus preventing deterioration of the parts and, at the same time, cooling the electrodes when necessary, (4) provision for adjustment of distance of holder from the spectrograph slit by an optical bench to permit variation in illuminating conditions, and (5) a hood for protection against light, fumes, and electric shock.

The design of the holder to be described is based on the suggestions of several operators and incorporates improvements found advisable by tests on a preliminary model.

II. DESIGN AND CONSTRUCTION

1. GENERAL FEATURES

A view of the holder, with the housing opened to expose the parts, is given in figure 2. Details of its design and construction are shown in the assembly drawing reproduced in figure 1. The holder consists of a heavy steel base, 1, standing on three legs (two V's and a flat) that rest on the optical bench. The base is locked to the bench by a claw, 2, and is fitted with a slide that is moved transversely by control, 3. The slide carries two steel upright rods, 4, that guide the electrode supports, 5. Each support consists of an H-shaped brass yoke, constructed from tubing and block brass, with a forward extension upon which is bolted a Bakelite plate, 6, carrying the electrode clamp, 7. The uprights, 4, are braced at the upper ends by a plate, 8, on which is mounted the upper control assembly, 9. This control provides vertical movement of the upper electrode support through miter gears and a screw, 10, threaded into the support. The screw chosen for this holder has a pitch of 1.5 mm. Precise setting of small electrode distances is provided by a drum, 11, mounted on the screw and graduated with 15 divisions, each division corresponding to a 0.1-mm travel of the electrode support. Independent motion of the lower electrode support is provided by a control, 12, with gears and a screw, 13, similar to the upper electrode assembly. The exposed metal parts, except the electrode clamps, are nickel-plated to resist corrosion.

2. ELECTRODE CLAMPS

Enlarged views of one of the electrode clamps are shown in section *D* of figure 1. The clamp jaws are made of two pieces of copper, one forming the movable jaw, 14, and the other the fixed jaw, 15. The motion of the jaw, 14, is precisely limited and controlled by a slide and ways on each side of the clamp. A quarter-turn of the knob, 18, provides the necessary opening and closing of the jaw ($\frac{1}{16}$ in.) through an eccentric shaft, 17. A spring, 20, provides a fixed tension on the jaw for clamping the electrodes. The clamp assembly extends through the opening between the holder uprights and terminates in a binding post for connection to electric power. The back cover, 22, of the eccentric and spring box is Bakelite, and the face cover, 23, exposed to the source is made of brass.

The electrode jaws are drilled to accommodate a variety of electrode diameters for the lower and upper clamps, respectively, as follows: $\frac{1}{2}$ in. vs $\frac{1}{2}$ in., $\frac{1}{4}$ in. vs $\frac{1}{8}$ in., $\frac{1}{4}$ in. vs $\frac{1}{4}$ in., and $\frac{7}{32}$ in. vs $\frac{7}{32}$ in. Slight variations from the standard electrode sizes cause no difficulty in clamping if the holes are made slightly oversize. Split cop-

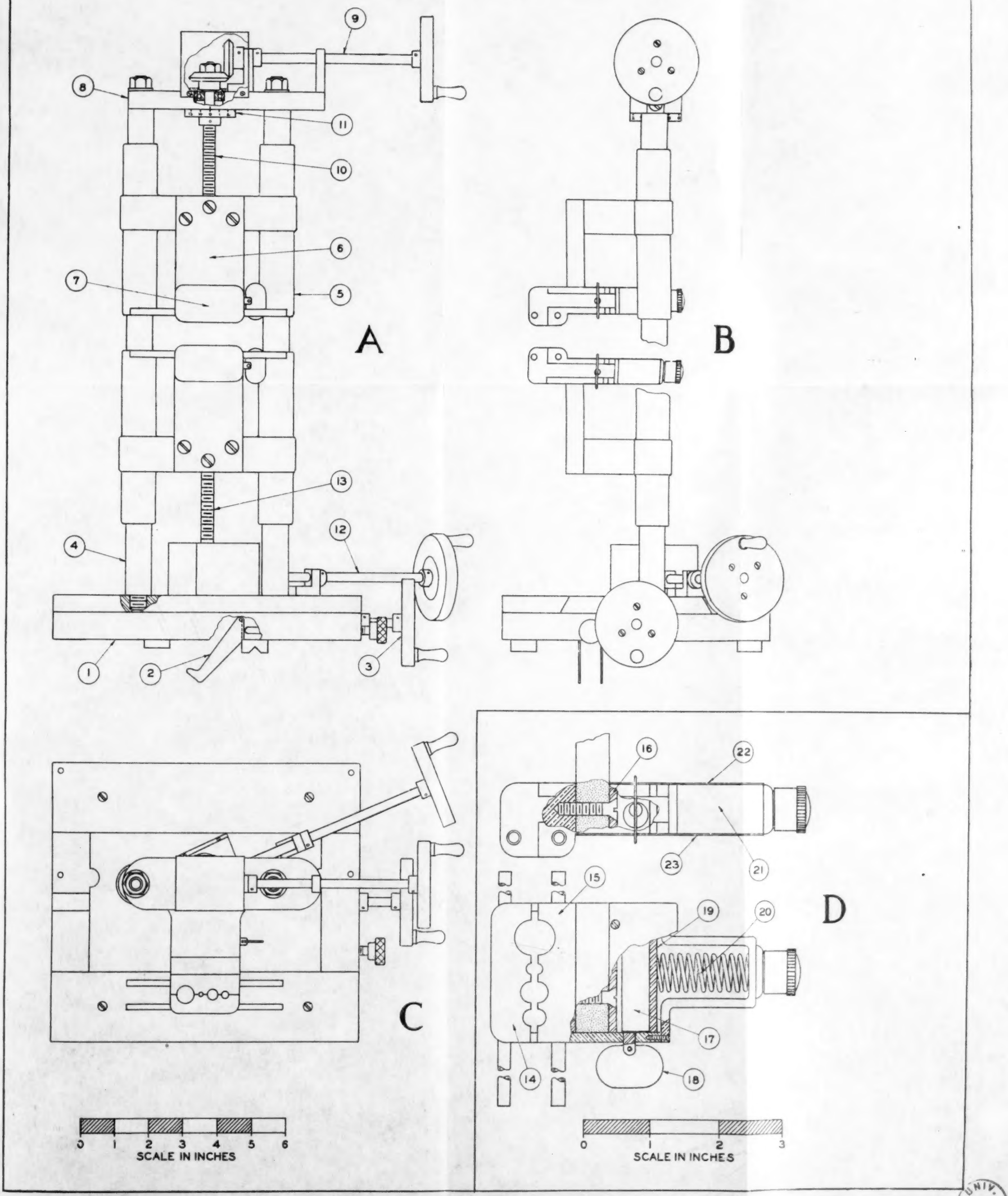

FIGURE 1.—*Assembly drawing of electrode holder.*

A, front view; *B*, side view; *C*, top view; *D*, detail of electrode clamp.

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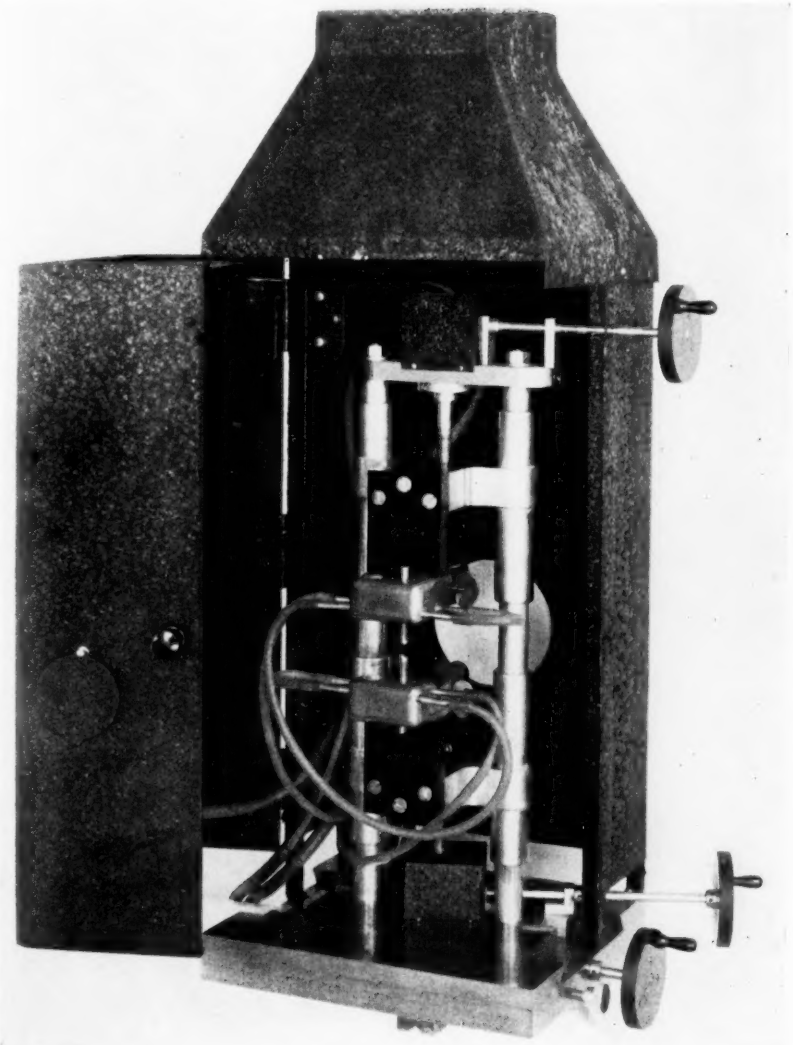

FIGURE 2.—*Improved electrode holder.*

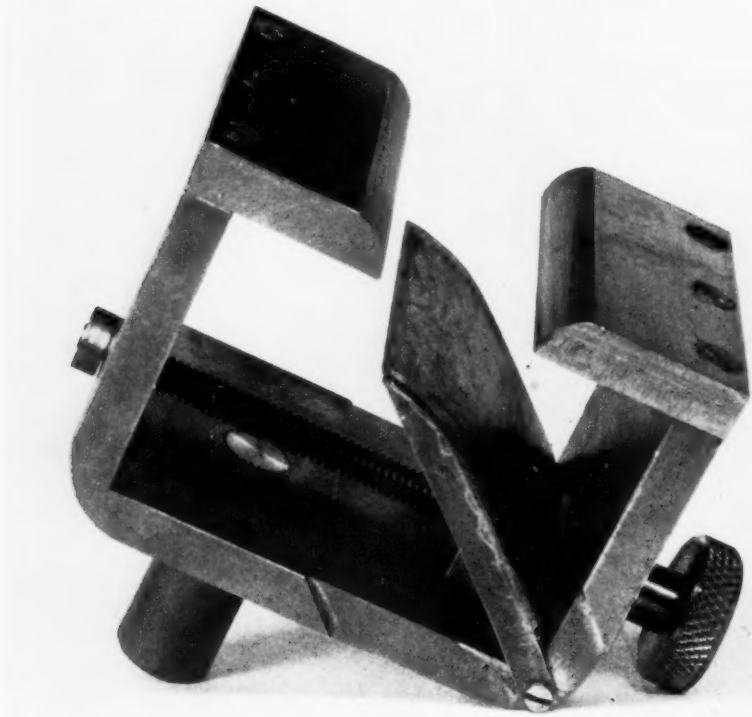

FIGURE 3.—*Accessory clamp for holding disk and sheet samples.*

per bushings, machined to fit the jaws, permit other electrode combinations. The jaws of the clamp, once accurately alined, have maintained alinement during continuous use. All corners and edges of the jaws are rounded and the parts streamlined to facilitate cleaning. Copper tubes inserted through the jaws serve for water circulation. Finally, an accessory clamp shown in figure 3, which accommodates flat bar, disk, or sheet samples, may be quickly locked into either the upper or lower electrode clamp.

3. WATER-COOLING SYSTEM

The electrode jaws are cooled by water circulated from a reservoir (5-gal bottle) by means of a small rotary pump, the water flowing successively through the four jaws of the clamps before returning to the reservoir. Connections in the water system are made by gum-rubber tubing and glass. This, combined with the use of distilled water in the system, is effective in preventing the leakage of high-voltage (35,000-v peak) power. The closed water system, always at room temperature or slightly higher, ensures freedom from condensation of moisture on the holder when not in use. As a convenience in operation, the pump motor is connected to power through a master switch which closes electric circuits to the spectrograph controls, a rotating sector, and a ventilator. Under these conditions the water-cooling system requires little attention from the operator.

4. HOUSING

The housing of the holder is built with a frame of ½-in. angle iron and a covering of galvanized sheet iron, and is finished in black crackle enamel. The forward half of the housing, which is supported on hinges at the side, forms a door to provide access to the holder. When the door is opened, a switch and safety circuit shut off the power circuit to the electrode clamps and a second switch closes a circuit to a lamp mounted in the corner of the door. The door opens to a stop so arranged that the lamp is placed in a position to project an image of the electrodes to a screen on the optical path for adjustment of the electrode positions. The lamp serves also to illuminate the interior of the housing.

Openings are cut in the front and back of the housing for the passage of light along the optical path. Ventilation is provided by a hood at the top of the housing, connected through a flexible tube to a ventilating system. A small upward current of air is sufficient; excessive air currents will make an arc discharge unsteady or even extinguish it. The housing is grounded through the base of the holder and the optical bench.

III. APPLICATIONS OF THE HOLDER

The holder has been employed for spark excitation with the various electrode combinations employed in the Bureau's spectroscopic laboratory. These include the spark between metal rods of sizes from ⅛ in. to ½ in. in diameter, between ⅛-in. graphite rod and flat metal specimens, and between pressed pellets ¼ in. in diameter and ¼ in. to ½ in. long. Cooling of the spark electrodes is useful when small electrodes or sheet-metal specimens are sparked. Sheet-metal samples may be mounted either vertically in the slot between the jaws

of the lower clamp or held horizontally in the accessory holder (fig. 3), with a supporting block of copper for rapid heat conduction. The sample in this case is opposed by a counter electrode of graphite. The holder has been found advantageous in establishing a reproducible condition of heat conduction from the electrodes. With holders previously used in this laboratory, considerable variation in conduction has been encountered, especially after deterioration of the holders in use.

Excitation by the a-c arc generally requires close control of alinement and gap distance of electrodes. In order to set the electrodes accurately for small gaps, the upper electrode is lowered almost in contact with the lower electrode, the clamp is opened slightly, permitting the upper electrode to drop into contact with the lower, the clamp is then released to grip the electrode, and, finally, the electrode is raised the required distance, which is measured on the graduated drum (fig. 1, part 11). The holder was found satisfactory not only in meeting the requirement of accuracy in the settings, but also in providing the advantage of cooling the electrodes. Small pellets or ⅛-in.-rod samples may be arced with little danger of overheating.

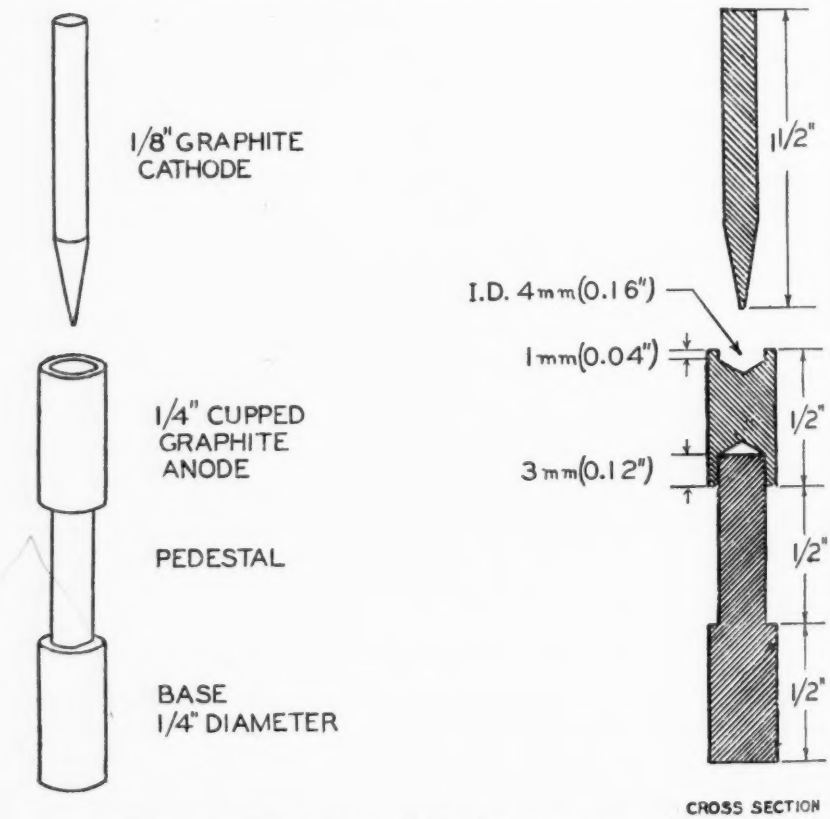

FIGURE 4.—*Electrode assembly for direct-current arc excitation.*

Direct-current arc excitation results both in radiation of heat and in evolution of hot, corrosive vapors. The design of the electrode clamps and efficient water cooling have proved effective in meeting these conditions for rapid and continuous use of the holder. The cooling of electrodes of various metals in the form of compressed pellets permits use of currents as high as 10 amp without danger of melting the electrode except at the end. However, if heat is required in the electrode, as in volatilizing samples from a hot graphite anode, unsatisfactory results may be observed with the customary electrode shapes. As a result of the high cooling efficiency of the holder, the electrodes are attacked only on the extreme ends with currents as high as 15 amp. To overcome this difficulty, the d-c arc electrode assembly was modified to provide an electrode combination that has proved adaptable to a number of applications of the d-c arc, both for the water-cooled holder and common clip holders. The assembly, with dimensions shown in figure 4, consists of a ⅛-in. upper cathode tapered to a point and a lower anode combination in two parts—first, a graphite base and pedestal supported in the electrode clamp; and, second, the electrode cap. The cap is drilled at both ends, the depth of the upper cup depending on the degree of heating required and the size of sample charge. By virtue of the low heat conductivity between the cap and the pedestal, the cap becomes very hot with only slight attack on the pedestal. This electrode combination gives reproducible excitation and requires a smaller quantity of graphite rod, which is a welcome economy when expensive high-purity electrodes must be used.

Experience with two of the improved electrode holders for numerous tests under various conditions shows that they have increased the speed of miscellaneous testing, provided more reproducible electrode orientation, and contributed to the safety and ease of operations.

The authors acknowledge the helpful suggestions of H. R. Mullin, of the Spectrographic Laboratory, and of Henry Philo, of the Bureau's Instrument Shop.

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Washington, October 22, 1942.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1516

Part of Journal of Research of the National Bureau of Standards, Volume 30, January 1943

NATURE OF THE REACTION OF WOOL WITH ALKALI

By Louis R. Mizell and Milton Harris [1]

ABSTRACT

The course of the reaction of the cystine in wool with alkali has been reinvestigated. The earlier findings that one sulfur atom is split from each molecule of cystine are confirmed. Of the residual noncystine sulfur in the alkali-treated wool, more than 25 percent has been accounted for as lanthionine. No significant amounts of sulfhydryl groups are in the treated wools. The results lead to the conclusion that the alkali cleavage of the disulfide group does not consist primarily in a hydrolytic rupture between the sulfur atoms with the formation of a sulfhydryl compound and a sulfenic acid, as postulated earlier; rather, they are more consistent with a mechanism recently advanced by Nicolet and Shinn, which involves a rupture between sulfur and carbon to yield dehydroalanine and a $-CH_2-S-SH$ residue. An atom of sulfur is then eliminated from the latter and the sulfhydryl group thus formed reacts with dehydroalanine to form lanthionine.

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I. INTRODUCTION

One of the most characteristic chemical properties of wool is the ease with which it is degraded in alkaline solutions. In earlier investigations [1, 2, 3][2] it was shown that such degradation is closely associated with the lability toward alkalies of the disulfide groups in the cystine of the wool. A study of the course of the degradation revealed that during the early stages, a rapid splitting off of a portion of the sulfur occurred, the amount of sulfur being lost closely approaching 50 percent of the original total [2]. This behavior led to the conclusion that the first step in the alkali degradation of wool is a splitting of the disulfide group to yield one labile and one comparatively stable sulfur group. Such a conclusion appeared to agree well with a view that had been proposed by Schöberl and Eck [4] to explain the lability of sulfur in various disulfides. According to these investigators, the cleavage of disulfides by alkali consists in a hydrolytic rupture of the disulfide

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate the literature references at the end of this paper.

linkage with the formation of a sulfhydryl compound and a sulfenic acid according to the following scheme:

$$R-CH_2-S-S-CH_2-R \longrightarrow RCH_2SH+HOSCH_2R. \quad (1)$$

The sulfenic acid, being extremely reactive and unstable in alkaline solution, immediately loses H_2S to form an aldehyde as follows:

$$RCH_2SOH \longrightarrow RCHO+H_2S. \quad (2)$$

Another possibility given consideration at that time was that proposed by Nicolet [5], who postulated that the removal of sulfur from cystine by alkalies takes place as an elimination of hydrogen sulfide from an intermediate enolized form according to the following equation:

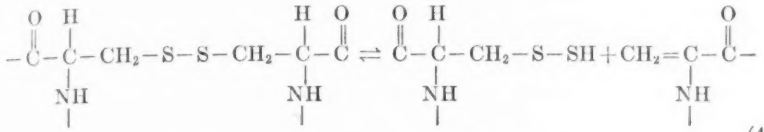
$$\begin{array}{l} CH_2-SH \\ | \\ CH-NH_2 \\ | \\ C=O \\ | \\ OH \end{array} \rightleftharpoons \begin{array}{l} CH_2-SH \\ | \\ C-NH_2 \\ \| \\ C-OH \\ | \\ OH \end{array} \longrightarrow \begin{array}{l} CH_2 \\ \| \\ C-NH_2+H_2S \\ | \\ C=O \\ | \\ OH \end{array} \quad (3)$$

He further suggested that from cystine, H_2S_2 would split out. Since this mechanism obviously failed to explain the loss of nearly half of the sulfur, little further attention was given to it.

Although Schöberl's hypothesis was consistent with the loss of about half of the sulfur, it failed to explain a number of other observed facts. For example, his explanation calls for the production of sulfhydryl and aldehyde groups, whereas tests for each of these groups on hydrolysates of the alkali-treated wool were definitely negative. As pointed out earlier [2], there existed the possibility that recombination between the aldehydic and sulfhydryl groups may have occurred under the conditions of the hydrolysis. However, it was subsequently shown [6] that few if any free sulfhydryl groups are present in the alkali-treated wool even prior to hydrolysis. In addition, this hypothesis, when applied to wool, would result in the rupture of the disulfide cross-links, a process which would be expected to yield a material of very low strength and extremely high alkali-solubility [7]. Yet samples of wool, treated with alkali by methods described elsewhere, exhibited relatively high strengths and low alkali-solubilities (see table 1). In fact, the properties of the alkali-treated wools were such as to strongly suggest that if the disulfide cross-links are destroyed, they are in a measure replaced by new linkages.

Considerable support for the view that new linkages can replace ruptured ones was found in the recent work of Horn, Jones, and Ringel [8], who succeeded in isolating from alkali-treated wool a sulfur-containing amino acid having the formula ($HOOC-CH(NH_2)-CH_2)_2S$, which they named lanthionine. Since practically all of the sulfur in undegraded wool can be accounted for as cystine sulfur, it seems certain that this new amino acid is a product of the reaction of the cystine in wool with alkali. More recently Nicolet and Shinn [9] have offered an explanation for the formation of lanthionine,

postulating as a primary reaction a split between carbon and sulfur as follows:



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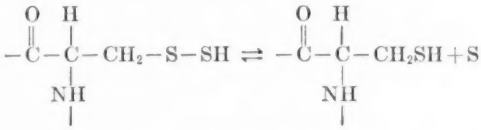

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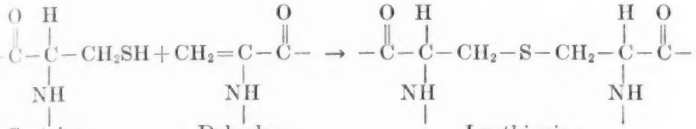

(6)

Cysteine Dehydro-alanine Lanthionine

This view has many advantages over the Schöberl hypothesis' since it not only explains the loss of half of the sulfur, but in addition it meets the requirements for linkage rebuilding and thus accounts for the relatively high strength and low alkali-solubility of alkali-treated wools. Finally, it offers an explanation for the absence of significant amounts of sulfhydryl and aldehyde groups in the wool hydrolysate.

On the basis of the new point of view resulting from the work of Horn, Jones, and Ringel, and that of Nicolet and Shinn, it appeared desirable to reinvestigate the course of the reaction of wool with alkalies.

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF ALKALI-TREATED WOOLS

The reported yields of lanthionine from alkali-treated wools (about 5 percent [8]) are low. While it is recognized that the values obtained by isolation methods are always low, nevertheless it should be possible to form larger amounts of this amino acid in the alkali-treated material if the reaction proceeds as suggested. On the basis of earlier work [2], it appears that sodium sulfide, one of the products of the reaction of wool with alkali, could interfere with the formation of lanthionine in either of two ways. It might compete with cysteine in the reaction with dehydroalanine (eq 3), or it could split unreacted disulfide linkages and thus lower the amount of dehydroalanine that could be produced.

In order to overcome this difficulty, resort was had to a flow method, in which a fresh solution of alkali, either at 0° or 50° C was allowed to flow continuously over the wool. Thus the reaction products were constantly washed from the fibers. In addition, by working at these lower temperatures instead of at the boiling point, secondary reac-

tions would be kept at a minimum. At the lower temperature, 350 g of wool were placed in a 12-liter flask fitted with an inlet and an outlet tube. The flask was immersed in a water bath at 0° C, and 0.1 *N* NaOH, precooled to 0° C, was continuously flowed over the wool for 600 hours at a rate of about 2 liters per hr. In the experiment at 50° C, 133 g of wool was placed loosely in a cheesecloth bag, attached to a plunger, and agitated in a monel-metal cylinder that contained about 10 liters of 0.1 *N* NaOH solution at 50° C±2°. Fresh solution at the same temperature was continually siphoned into the bottom of the cylinder at a rate of about 12 liters per hour for 8 hr. The liquid in the cylinder was maintained at a constant level by removing the spent solution as rapidly as the fresh solution was introduced.

At the end of each treatment, the samples were removed from the alkali and washed with distilled water. A sodium nitroprusside test, used for the qualitative detection of sulfhydryl groups, was negative on both samples. Immediately after the washing treatment, small portions of the wools were treated with benzyl chloride [7] in order to combine any cysteine residues that might be present.

2. ANALYTICAL PROCEDURES

The cystine analyses were made by the Sullivan method [10], sulfur analyses by the oxygen-bomb method [11], alkali-solubilities by the method of Harris and Smith [12], and serine analyses by the method of Nicolet and Shinn [13].

3. ISOLATION OF LANTHIONINE

Lanthionine was isolated from the alkali-treated wool by a slight modification of the procedure described by Horn, Jones and Ringel [8]. The modification was to remove residual cystine from the residue containing the water-insoluble amino acids, and the method was carried out as follows. The residue was taken up in 150 ml of water and concentrated ammonium hydroxide was added dropwise until the residue was completely dissolved. One and one-half grams of sodium cyanide was then added to the solution, and the mixture was allowed to stand 1 hr, after which it was made acid to litmus by the addition of acetic acid. The solution was kept in a refrigerator for 48 hr, and the crystals which formed were filtered off. The filtrate was concentrated in a vacuum and allowed to stand in a refrigerator for 3 days and the crystals again collected. A third batch of crystals was obtained by again concentrating the filtrate. The crystalline precipitates were combined and further purified by suspension in 50 ml of water and by adding concentrated NH_4OH dropwise until the solution was complete. A small amount of impurities was filtered off, and on acidifying the solution with acetic acid, a precipitate of wedge-shaped plates [8] was obtained. Analyses on the material were as follows:

		C	H	S
Calculated	%	34.59	5.81	15.41
Found	%	34.09	5.70	15.30

III. RESULTS AND DISCUSSION

The effects of the treatments with alkali by the flow method are shown in table 1. Confirming earlier findings, it is seen that there is good agreement between the experimental values for the cystine contents of the treated wools and those calculated on the assumption that a molecule of cystine is destroyed for each atom of sulfur lost. That little, if any, free cysteine is in the alkali-treated wools is indicated by the values for the samples alkylated with benzyl chloride. This follows from the fact that in the Sullivan method both cystine and cysteine are determined, but not thioethers such as would be derived from the reaction of cysteine with benzyl chloride. Had any appreciable amounts of cysteine been present, the cystine values for those samples treated with benzyl chloride would have been much lower.

TABLE 1.—*Effect on wool of treatment with alkali by the flow method*

Sample	Cystine		Total sulfur	Alkali-solubility	Serine
	Found	Calculated [1]			
0.1 *N* NaOH flow for 600 hours at 0° C					
	%	%	%	%	%
Untreated	11.3		3.50	10.5	9.5
Treated	4.4	3.1	2.40	5.0	9.4
Treated+$C_6H_5CH_2Cl$	4.2				
0.1 *N* NaOH flow for 8 hours at 50° C					
Untreated	12.5		3.50		
Treated	2.7	1.1	1.98		
Treated+$C_6H_5CH_2Cl$	2.5				

[1] Calculated on the basis that each atom of sulfur lost by the wool represents the destruction of 1 molecule of cystine.

The question as to the fate of the residual noncystine sulfur in the treated wool arises. Earlier [2] it was suggested that a stable thiocompound was formed. Thus, for example, if the view of Schöberl were correct, a thioacetal could be formed. On the other hand, if lanthionine is the end product, the original mechanism postulated by Schöberl would not hold. As pointed out previously, however, the reported yields of lanthionine have been so low that there would be serious objections to the assumption that the alkali-degradation of the cystine in wool resulted principally in the formation of lanthionine as an end product.

In the present investigation, considerably higher yields of lanthionine were obtained. From a 94.7-g sample of wool that had been treated for 600 hr at 0° C, 1.47 g of lanthionine was obtained. Since, as seen from table 1, the cystine content of this sample had decreased 6.9 percent, a theoretical yield of 5.67 g of lanthionine might have been expected. The actual yield was thus 25.5 percent. Similarly, 2.2 g of a theoretical 7.7 g of lanthionine (28.8-percent yield) was obtained from the sample treated for 8 hr at 50° C. While these results ac-

count only for somewhat more than one-fourth of the sulfur which is no longer present as cystine, nevertheless, the amount is appreciable and, in view of the difficulties involved in the isolation technique, serious consideration must be given to the possibility that lanthionine may be a principal end product in the reaction of the cystine in wool with alkali.[3]

It should be pointed out that lanthionine might conceivably be formed by the reaction of cysteine with a dehydroalanine residue which might be formed from the reaction of the serine in wool with alkali [9]. That this was not the case is indicated by the data in the last column of table 1, which show that at 0° C the original content of serine has not been altered by the alkali treatment.

If, as the results of the present investigation indicate, an appreciable amount of sulfhydryl groups is not present in the alkali-treated wool, there still remains to be explained the apparent abnormal base-binding capacity of wool. It will be recalled that wool fails to reach equilibrium with alkaline solutions in titration experiments, a fact that was attributed [14] to the reaction of the base with the disulfide groups of the cystine. More specifically, on the assumption that the cleavage proceeds according to the Schöberl hypothesis, it was postulated that the "extra" base was bound by sulfhydryl groups (eq 1). Obviously, this postulate is no longer valid and a new explanation must be sought. The earlier titration experiments indicated that the apparent "extra" base bound was equivalent to the sulfur which split from the wool. In light of Nicolet's hypothesis (eq 4, 5, and 6), the phenomena could be accounted for if the sulfur which is split from the wool (eq 5) reacted with base in such a way as to consume 1 equivalent of base per sulfur atom. In order to test this possibility, 0.0109 g of sulfur was dissolved in 20 ml of ethyl alcohol [4] and the solution mixed with 20 ml of 0.1242 *N* sodium hydroxide. The solution was kept at 25° C and aliquots withdrawn at intervals, and titrated with standard hydrochloric acid. The results are given in table 2.

TABLE 2.—*Reaction of sodium hydroxide with sulfur (0.0109 g) at 25° C*

Time	Total NaOH present	NaOH consumed	NaOH consumed per *M-eq* of sulfur
hr	*M-eq*	*M-eq*	*M-eq*
0	2.48		
1	2.32	0.16	0.50
20	2.19	.29	.87
48	2.18	.30	.89
115	2.18	.30	.89

It will be seen that nearly 1 equivalent of sodium hydroxide per atom of sulfur has been consumed. While the nature of reaction of sulfur with sodium hydroxide is not clear, nevertheless, the results are sufficiently close as to be able to account for the so-called "extra" base take-up in titration experiments. Finally, it may be pointed out that the results of these titration experiments, although constituting

[3] This suggests that the permanent set, of the type produced by treating wool fibers with alkali, may result in part from the formation of lanthionine. Such a possibility has already been pointed out by Speakman and Whewell [3], since they have suggested that —C—S—C— bonds might be formed under these conditions.

[4] Sulfur is not readily soluble in dilute NaOH. In the degradation of the cystine in wool, atomic sulfur is involved and would immediately go into solution.

only indirect evidence, may be considered as further support for the reaction proposed by Nicolet and Shinn.

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PHOTOCHEMICAL STABILITY OF PAPERS

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ABSTRACT

Papers were irradiated with a carbon arc through a filter that completely eliminated infrared, and ultraviolet shorter than approximately 330 millimicrons. Sheet temperature was kept near 30° C during irradiation, through contact with a thermostated metal backing, thereby eliminating heat effects, shown otherwise to overshadow light effects, using intense sources.

In consequence, the results differed from those of previous workers. Yellowing of papers (without lignin) commonly ascribed to light was found to result from heat or age, but not light; papers bleached when heat effects were eliminated during irradiation. Even lignified paper was bleached by light in nitrogen.

Paper scorched brown at high temperatures or yellowed at 100° C, and yellow papers 250 years old were bleached by light.

Lack of oxygen inhibits but does not altogether prevent photochemical deterioration. The role of water vapor differs fundamentally for cotton and wood-pulp paper.

Lignified paper is very unstable to light. Printers' ink extensively protects paper.

Irradiated papers are subsequently less stable in the dark than those not previously irradiated.

The order of photochemical stability of papers was as follows: new-rag, refined sulfite, old-rag, soda-sulfite, and newsprint. The light stability of new-rag papers was greatly affected by acid and rosin, whereas that of old-rag and soda-sulfite was only slightly affected, in contrast to heat stability, for which pH is important for all fibers. Newsprint, made neutral with $NaHCO_3$, showed a large increase in light stability. Rosin did not seriously affect the stability of any papers as long as their acidity was low.

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I. INTRODUCTION

The effect of light upon paper is one of the most important problems in the preservation of valuable records. Irreplaceable documents are being exhibited under conditions which may be unnecessarily adverse. This investigation was undertaken as a part of the general program of research at the National Bureau of Standards for the preservation of records, and deals with the factors influencing the light stability of white record papers, not only as regards atmospheric conditions but also with respect to paper components. A third phase of the subject, namely, the relative deterioration occurring at various wavelengths of the spectrum to which papers are ordinarily exposed, is still in the process of investigation.

The stability of papers toward various types of light has been the subject of previous investigations. Richter [1] [1] exposed a variety of papers, differing in kinds of fiber and sizing, to direct sunlight, and in a few experiments to a quartz-mercury arc, and measured the consequent changes in folding endurance, and to a lesser extent, changes in chemical characteristics. Edge and McKenzie [2] measured changes in the reflectance of wood-pulp papers exposed to direct sunlight, a quartz-mercury arc, and a carbon arc. Oguri [3] measured the changes in copper number of a tissue paper and a filter paper caused by a quartz-mercury arc. The effect of sunlight upon newsprint was studied by Bakker [4].

It is evident, however, that these types of light do not correspond to the light to which papers are normally subjected, namely, diffused indirect daylight transmitted by window glass or tungsten incandescent-lamp light. The exact duplication of sky light as transmitted by window glass is not necessary for a study of the effects of normal lighting upon papers, nevertheless, certain objectionable characteristics of direct sunlight or of the usual high-intensity sources can be eliminated. The ultraviolet region of sunlight extending from 290 to 330 millimicrons, shown by Richter [1] to account for almost half of the effect of sunlight upon paper, is normally excluded by window glass and, therefore, has no counterpart in interior daylight. Also, Oguri [3] has shown that over 90 percent of the radiant energy from a quartz-mercury arc harmful to paper is excluded by window glass.

Intense sources, including direct sunlight, furthermore, give rise to temperature effects which have no counterpart in interior daylight. The high temperatures attained by sheets of paper during irradiation with powerful light sources was discussed by one of the writers elsewhere [5].

Köhler [6] exposed some papers covered with various colored glasses to north sky light, as well as to direct sunlight, and thus, in the former procedure, avoided the objection mentioned. The purpose of his investigation, however, was to select a protective window glass for the Archives at Stockholm from various commercial products rather than a study of factors affecting the stability of papers. The study was limited to three papers, for which changes in folding endurance were measured. Changes in copper number for one paper during the 128-day period of exposure were also measured. The changes during this period were quite large owing to the rather poor quality of papers used, since the best, a rag paper, had an initial copper number of 1.6.

[1] Figures in brackets indicate the literature references at the end of this paper.

In the present investigation a large number of experimental book and writing papers produced in the paper mill at the Bureau, as well as commercial newsprint paper, were irradiated under conditions that were rigidly controlled. The papers, which embodied large differences in kind and quality of fiber, content of lignin, rosin, and other sizing materials, acid, and filler, were maintained near 30° C (30° to 32°) during irradiation. All unusually short and long wavelengths were excluded by a special filter combination. The relative humidity was fixed at a definite value, except when moisture or oxygen content was intentionally varied.

In the present work, it is believed that the conditions under which light usually affects white record papers have been attained more nearly than heretofore, and that the results dealing with the factors influencing the light stability, the permanence of papers once exposed to light, and the color changes in papers caused by light, are representative of the behavior of record papers under the most prevalent conditions of use.

II. APPARATUS

A commercial arc lamp with ½-inch electrodes of solid carbon, enclosed in Pyrex, operating at 2,080 watts and 16.5 amperes, was used in all experiments. The flame of the arc was 15.8 cm from the center of the sheet during irradiation. In combination with this lamp, a liquid filter [5] consisting of a glass cell, made up of one sheet of Corex-*D* glass and one sheet of ordinary window glass, and through which was pumped a 0.117-*M* solution of cupric chloride to remove the infrared, was used. The radiant energy thus reaching the papers consisted essentially of the strong cyanogen band at 389 millimicrons [7] superposed on a black-body continuum arising from the incandescent positive electrode, and did not include any radiant energy having a wavelength shorter than approximately 330 nor longer than 750 millimicrons.

The spectral distribution of this light and that of the sky light [2] entering the laboratory through windows was studied by the method of transmission through glass filters having sharp cut-offs and known spectral-transmission curves. A two-photocell balanced circuit with potentiometer (for the arc light, an automatic-recording potentiometer) was used for measuring transmissions. It was found that 80 percent of the filtered arc light lay in the region between approximately 330 and 440 millimicrons. Of the sky light, 25 percent was found to lie in this region and less than 0.1 percent in the infrared region beyond 750 millimicrons.

Inasmuch as the light usually affecting papers is in the region [3] between approximately 330 and 440 millimicrons, and since the filtered arc light included neither the shorter ultraviolet nor infrared, it is probable that the light used in this work differed from normal lighting in its effect upon papers mainly in intensity.

The remainder of the apparatus and its effectiveness are described in detail in a paper by one of the writers [5]. Principal emphasis was placed on control of the temperature of the paper during irradiation. The temperature of the sheets was maintained near 30° C by intimate contact, through suction, with a thermostated aluminum backing,

[2] Eastern sky at 2:15 p. m. on a clear day (April 23, 1942).
[3] Unpublished findings by the present writers.

supplemented by the removal of most of the undesired infrared. The air which continually flowed through the sheets during irradiation was kept at constant moisture content corresponding to a relative humidity of 58 percent at 30° C. For experiments in which moisture was practically excluded, the air was dried to a relative humidity not higher than 0.015 percent by continuous circulation over anhydrous magnesium perchlorate. For experiments in which oxygen was practically excluded, dry nitrogen was continuously circulated over copper gauze at 500° C, giving a content of O_2 of less than 0.03 percent. For one experiment the content of O_2 was probably much lower than this figure, since a small glass irradiation chamber was substituted for the usual large one to reduce leakage of O_2 into the system by diffusion.

These were the usual conditions of irradiation. In a few comparison experiments the cupric chloride cell and paper thermostating arrangement were omitted. The distance from the arc to the sheet was changed in certain experiments. Papers were usually irradiated on one side of the sheet, although in many experiments both sides were irradiated. Departures from the usual conditions are stated in each instance.

III. SAMPLES STUDIED AND METHODS OF ANALYSIS

Thirty-one representative white, undyed book and writing papers produced in the semicommercial paper mill at the National Bureau of Standards from a variety of commercial materials were used for study. The pertinent characteristics of the papers are listed in the tables accompanying this publication. The papermaking details were given in other publications of the Paper Section [8]. One commercial newsprint paper was also included in the study. This paper may be considered as representative of highly lignified papers in general, and was very useful because of the large chemical changes caused in it by relatively mild exposures to light. Some very old commercial papers were used in a few experiments.

The names of the various types of papers used in the investigation are those current in the paper industry and probably require definition. "New rag" is obtained from unused cotton fabric and represents a type of cellulose with relatively large stable molecules. "Old rag" is used cotton fabric which has been bleached, often drastically, to remove colors, and represents a type of cellulose with smaller molecules arising from this treatment and from the wear and washing of the fabric as a garment. Soda and sulfite pulps are produced from wood by alkaline and acid treatments, respectively, to remove lignin. These represent the cheaper grades of pulps used for record papers and contain substances other than cellulose, which produce yellowing and deterioration of the paper with age. "Refined" sulfite, therefore, is sulfite pulp which has been subjected to treatments designed to remove the substances other than cellulose, and is thus a more stable material. Newsprint consists largely of ground wood containing the original lignin.

Various test methods to determine the extent of deterioration caused by light were employed. The volumetric alpha-cellulose method was found to be the most generally useful. pH (cold extract) and resin were also determined. These three methods are described

elsewhere by one of the writers [9]. Fluidities of dispersions of cellulose in cuprammonium solution were measured [10] in a number of instances. Copper number and folding endurance [11] were also determined.

Since the values for copper number merely substantiated the alpha-cellulose results, they are omitted except in a few cases of particular interest. The values for folding endurance are also omitted, inasmuch as they also substantiated the alpha-cellulose results, but with far less precision, owing to the nature of the test. In general, after 17 hours of irradiation the rag papers had retentions of folding endurance upward of 75 percent, whereas the soda-sulfite papers ranged between 50 and 85 percent.

Although the alpha-cellulose results, as determined by the method employed, are practically independent of the presence of lignin in most analyses, this fact had to be confirmed for control analysis for the action of light. Therefore, a sample of irradiated newsprint was analyzed for alpha cellulose by both the volumetric and gravimetric method. Since in the gravimetric method the amount of lignin present must be corrected for, the lignin content was determined by the method of Ritter and Barbour [12]. Certain other lignin analyses were also carried out, using this method. Starch and glue [11] were also determined in a few instances.

The irradiated area of each sheet was 20 by 20 cm. pH, resin, and folding endurance were determined from strips; other tests were made on ground papers. Two, and often three, sheets of the same paper were irradiated, one at a time, to make possible all of the tests desired and to check and sometimes recheck experimental results.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. CHANGES IN PAPERS DURING IRRADIATION WITH AND WITHOUT TEMPERATURE CONTROL OF SHEETS

Inasmuch as stress in this investigation was laid upon the study of effects of light alone, as contrasted with the light-plus-heat effects usually obtained with intense sources, including direct sunlight, it is of interest to compare changes in papers during irradiation under these two conditions. It was previously shown [5] that various sheet materials, including paper, attain abnormally high temperatures when irradiated with a commercial carbon-arc lamp under conditions similar to those of the usual "light" stability tests.

(a) CHEMICAL DETERIORATION BY HEAT DURING IRRADIATION

Two series of experiments were conducted which differed essentially in that the temperatures of the sheets were maintained near 30° C in one series, thus precluding measurable thermal deterioration, whereas in the other series the temperatures were not controlled.

The sheets in both series were placed 25 cm from the flame of a Pyrex-enclosed carbon arc operating at 2,080 watts. No attempt was made to exclude the infrared in these experiments. The radiant intensity incident upon the sheets was 0.4 watt/cm^2, as measured with a calibrated thermopile-recorder system, described elsewhere by one of the writers [5, 13].

The results presented in table 1 show that extensive deterioration due to heat took place if the sheet temperatures were not controlled during irradiation with an arc lamp. The effect of heat may be several or many times greater than that of light.

TABLE 1.—*Predominance of heat effects over light effects during irradiation* [a] *with the carbon-arc lamp when sheet temperatures are not controlled*

Paper number [b]	Decrease in alpha-cellulose percentage	
	Sheets freely suspended. No temperature control [c]	Sheets in intimate contact with aluminum backing. Temperature near 30° C
1129 (soda-sulfite)	54.7	3.6
1134 (soda-sulfite)	31.2	3.8
1191 (old rag)	4.5	1.1
1215 (old rag)	3.7	1.3

[a] The papers were irradiated for 17 hours at a distance of 25 cm from the arc and with the same incident radiant intensity in each experiment. The moisture content of the sheets was not controlled. See text for further details.

[b] See table 3 for further details of these papers.

[c] From the results previously published by one of the writers [5], it is estimated that the temperature attained by the sheets under these conditions was between 160° and 200° C.

(b) COLOR CHANGES ARISING FROM HEAT AND FROM LIGHT

The yellowing of paper upon exposure to "light" is a familiar phenomenon. Richter [1] reported a yellowing of all the types of papers studied, including rag, purified and ordinary wood pulp, sized and unsized, during a 100-hour exposure to Miami, Fla. autumn sunlight. Sunlight, however, was used in the early days of papermaking to bleach papers.

These opposite effects, bleaching and yellowing, were observed by Edge and McKenzie [2] with papers made from wood pulp and irradiated with sunlight. For eight papers, sunlight in England caused much more bleaching and less yellowing than the sunlight in the warmer and more humid Cairo, Egypt. Portions of the papers exposed in Cairo had been covered with an opaque paper. These covered portions, which were thus subjected to approximately the same heating as the exposed portions, yellowed more than the exposed portions. Specimens of the same papers, when exposed to a quartz-mercury or carbon arc, yellowed extensively.

In the present investigation it was found that all of the papers, excepting one containing appreciable quantities of lignin, bleached when irradiated in air when the temperature was maintained near 30° C during irradiation, but all of them yellowed during irradiation when the temperature was not controlled.

A typical example of these two opposing effects is shown in figure 1 for paper 1129. Both sheets *A* and *B* were irradiated at 25 cm from the flame of the same Pyrex-enclosed arc. Sheet *A* was maintained near 30° C; sheet *B* was freely suspended without temperature control, as in the usual commercial "light" stability testing equipment. The extent of yellowing or bleaching was determined by measuring the reflectance of a particular area of each sheet for violet-blue light (the

405- and 436-millimicron Hg lines, together) in an apparatus previously described elsewhere [14].

The two competing processes, bleaching and yellowing, are thus shown to have occurred simultaneously, the net observable effect indicating whether light or heat changes predominated. Thus, if a white paper turns yellow when irradiated, it may be inferred that

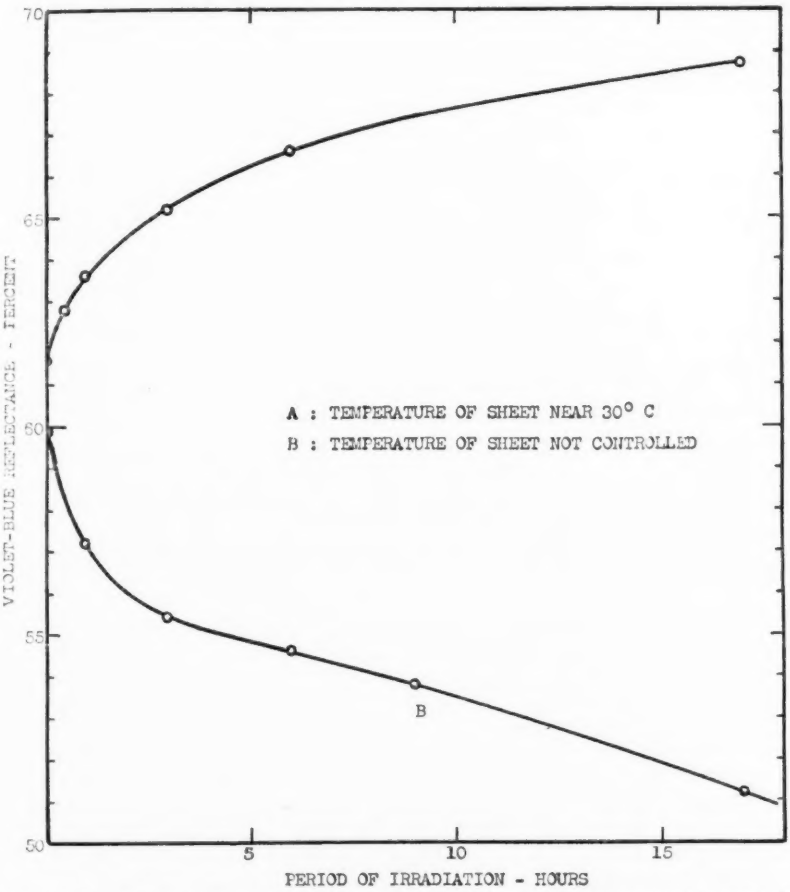

FIGURE 1.—*Color changes in paper irradiated with and without temperature control, using the carbon arc.*

reactions other than photochemical ones have played the dominant role.

These remarks do not apply to papers containing appreciable quantities of lignin, for this material caused yellowing of paper even in the absence of heat effects. Extensive yellowing occurred in newsprint when irradiated under the usual conditions at 30° C in air. This yellowing resulted from the lignin and was obviously different from the yellowing of cotton fibers containing no lignin, or the yellowing of delignified wood fibers, such as in paper 1129 and the other soda-

sulfite papers which contained less than 0.5 percent of lignin. However, when the yellowing due to lignin was prevented by lack of oxygen the cellulose fibers in newsprint were bleached by light. This yellowing and bleaching of newsprint by light is shown in table 2, experiments *N* and *N*-no O_2.[4]

TABLE 2.—*Effect of light and heat upon the violet-blue reflectance*[a] *of papers*

Paper number and experimental condition	Kind of paper	Effect of light,[b] then heat,[c] on reflectance			Effect of heat, then light, on reflectance		
		Original	Light 40 hours[d]	Heat	Original	Heat	Light 17 hours
		%	%	%	%	%	%
1138	Soda-sulfite	[e] 61.2	71.3	58.1	[e] 63.6	56.8	66.6
1138-no H_2O	do	[e] 61.2	63.2	49.7			
1138-no O_2	do	[e] 59.2	62.8	54.2			
1133	do	55.5	66.6	59.2	55.5	52.6	
1143	do	56.7	66.1		57.0	53.2	62.0
1173	do	70.6	79.1		69.6	65.7	
1182	New rag	74.2	77.2	68.8	74.2	69.2	75.1
1183	do	75.8	77.6	71.3	75.8	72.5	
1203	Old rag	73.3	77.4	69.3	73.4	69.1	75.8
1215	do	77.9	80.8		78.0	77.0	
1164	Refined sulfite	73.6	76.1	70.5	73.8	70.4	70.8
1166	do	73.2	75.6	69.8			
N	Newsprint	46.0	34.0				
N-no O_2	do	45.8	51.0				
p-1700	Rag, very old	32.0	53.4				
p-1791	do	46.8	65.7				
p-280°	Sulfite, scorched	36.0	53.7				

[a] The reflectance at 45° from normal incidence, for the combination of the two mercury lines, 405 and 436 millimicrons, was measured as described in a previous publication [14].

[b] The light was that of the arc lamp under the usual conditions of irradiation, for the time periods given at the head of the two columns, excepting newsprint, which was irradiated for 10 hours in these experiments.

[c] All heating took place in air in the dark at 100° C for 72 hours.

[d] 20 hours on each side of sheet.

[e] These values are the reflectances of a particular area, 30 by 58 mm, of different sheets of the same paper. The measurements were always confined to exactly the same area, and the values were reproducible to within 0.2 percent reflectance.

It was found that mild heating yellowed all of the types of papers, especially those that had been bleached previously by light. Table 2 shows the yellowing produced in papers by heating at 100° C for 72 hours in a dark oven. The color changes correspond, in general, to other chemical changes caused by heat: 1133 showed the smallest color change and also the lowest change in alpha-cellulose percentage (some alpha-cellulose changes caused by heat are given in table 12).

It is of interest to note from table 2 that the yellow color caused by heat could be bleached out again by light, and that the bleaching caused by light could be nullified by heat, depending upon which process predominated.

The yellowing effect of heat was found to be large if the paper was previously (or concurrently) irradiated, especially if the irradiation took place in the absence of water vapor, as in experiment 1138-no H_2O. In this instance, the area of the sheet which had been exposed to light turned much yellower during heating than the borders of the sheet which had not been exposed to light, since they were covered by the clamping mechanism during irradiation.

Thus papers which are irradiated with strong light sources, including sunlight, without effective temperature control of the sheet, yellow

[4] An extremely low concentration of oxygen was probably attained in the latter experiment, since the irradiation took place in a small, all-glass chamber which was substituted for the large chamber usually used [5]. The former experiment, with air, was also performed in this apparatus for purposes of comparison. In both cases, the usual stream of conditioned circulating gas served to cool the rather limited area of paper.

owing to heat, assisted by the desiccation caused by the heat prevailing in the sheet during irradiation.

Another sheet of 1138 which had been irradiated in the absence of water vapor and then not used for further experimentation was stored in a cool, dark place. After 15 months it was found to have yellowed markedly in the areas that had been irradiated, but not in those covered by the clamping mechanism during irradiation. In this instance, age instead of heat had caused the irradiated paper to yellow. This probably explains the yellowing observed by Köhler [6] in papers exposed for 128 days to north sky light, under which conditions heat effects were probably negligible. Thus light did not cause papers (containing no lignin) to yellow, but the irradiated fibers underwent relatively rapid changes with age—more rapidly at higher temperatures—which were not photochemical and which confuse the study of the direct effect of light upon paper. This stresses the fact that direct-light effects must be studied not only in the absence of heat effects, but also in the absence of age effects, i. e., the light must be of sufficient intensity to cause a change rapidly enough to render concurrent age effects negligible.

Water vapor and oxygen were found to play an important part in the bleaching of paper by light, inasmuch as the lack of these gases greatly decreased the extent of bleaching in experiments 1138-no H_2O and 1138-no O_2, although other reactions were not inhibited by the lack of water vapor, as seen from the subsequent extensive yellowing by heating. Paper 1138-no O_2 yellowed much the same upon subsequent heating as if it had not been previously irradiated (see 1138, column 6 of table 2).

The bleaching effect of light was observed also in the case of papers yellowed with relatively great age or scorched at high temperatures. One paper, manufactured before the year 1700, was of a blotched brown; another, made before 1791, was of an even, deep-yellow color; and a third was an experimental hand sheet made from refined sulfite pulp, containing a thermojunction to permit measurement of the sheet temperature on exposure to a carbon-arc lamp. This third paper had attained a temperature of 280° C, as shown in a previous publication [5], and had been scorched to a brown color in a few minutes. These three papers, when exposed to the light at 30° C, bleached extensively. The scorched paper nearly regained its original whiteness, whereas the second paper became as white as a bleached new-rag paper. The three papers with color changes are listed in table 2 as *p*-1700, *p*-1791, and *p*-280°, respectively.

This effect may have practical significance for documents discolored by age or heat; bleaching may greatly heighten the contrast and permit more legible photographs to be made. This method of bleaching, of course, has the drawback that the light concurrently causes deterioration of the cellulose.

2. EFFECT OF VARIOUS FACTORS UPON THE LIGHT STABILITY OF PAPERS

(a) AMOUNT OF LIGHT ABSORBED AND METHOD OF ITS MEASUREMENT

Only the light absorbed by a sheet of paper can cause deterioration, the extent of which is a function of the amount of light absorbed, all other factors being equal. Values for the percentage of light absorp-

tion and decreases in alpha-cellulose percentage for the papers are listed in table 3.

TABLE 3.—*Influence of various factors upon the light stability of papers* [a]

Paper no.[b]	Filler, etc.	Rosin[c]	pH[d]	Light absorption	Decrease in alpha-cellulose[e] percentage during irradiation for—		Lowering of pH[g]
					17 hr	40 hr[f]	
	PAPERS MADE FROM NEW RAGS						
		%		%			
1177	10 to 13% clay	0	5.6	12	1.0	2.0	0.0
1178	do	0	5.1	12	1.6	4.0	.0
1179	do	1.4	6.0	21	1.0	2.6	.2
1182	do	1.5	4.8	20	4.2	5.5	.3
1183	do	0.6	5.8	15	1.7	3.4	.5
1186	do	.7	4.8	21	3.0	3.7	.1
991	None	0	6.9	10	0.8		.4
991	None; 2.1% glue	0	6.1	13	1.1		.4
1013	None	1.0	6.2	16	1.2		.8
1013	None; 1.9% glue	1.0	5.6	17	1.4		.6
1013	None; 1.8% starch	1.0	5.8	13	1.0		.5
	PAPERS MADE FROM OLD RAGS						
1191	12% clay	0	6.8	16	3.2	5.3	0.4
1193	do	0	5.0	16	2.9	6.2	
1200	do	1.2	6.1	18	3.5	6.2	.8
1203	do	1.3	5.2	23	4.0	7.1	.3
1214	None	0.3	5.8	21	3.4		
1215	14% $CaCO_3$	0	9.4	12	3.3	4.6	
1209	4.2% TiO_2, 8.4% $BaSO_4$	.6	5.0	25	2.2		
1211	7.2% ZnS, 5.8% $BaSO_4$	.7	6.0	26	4.7		
	PAPERS MADE FROM SODA AND SULFITE (1:1) PULPS						
1133	None	0	6.4	34	5.6	6.8	0.0
1134	8 to 10% clay	0	6.1	32	5.3	9.5	.3
1129	do	0	4.8	32	5.1	9.5	.2
1143	None	.6	5.6	35	5.8	9.5	.6
1136	8 to 10% clay	.9	5.8	30	7.0	10.9	.4
1138	do	1.6	4.9	30	6.2	10.4	.4
1173	21% $CaCO_3$	1.3	8.8	28	5.1	7.8	
1144	7% TiO_2	0.6	5.4	29	5.8		
1153	6.2% ZnS, 5.1% $BaSO_4$	.9	5.2	34	5.7		
	PAPERS MADE FROM REFINED SULFITE PULP						
1160	8 to 11% clay	0	6.6	16	1.3	2.7	0.3
1164	do	.9	5.6	21	2.4	5.2	
1166	do	.8	4.8	22	2.9	4.7	.3
	PAPERS MADE FROM HIGHLY LIGNIFIED FIBERS (NEWSPRINT)						
N-a	None		5.0	60	31.3		1.7
N-b	$NaHCO_3$ added		7.2	65	9.3		

[a] Sheets maintained at 30° C in air at 58% relative humidity.
[b] For other characteristics of the papers, see reference [8].
[c] Analytical resin values corrected for natural resins, fats, waxes, etc.
[d] pH of the cold-water extract of unirradiated sheets.
[e] To permit comparison with the results of other workers, increases in copper numbers for representative papers during 40 hours of irradiation are included as follows: No. 1136, 3.2; No. 1164, 1.6; No. 1182, 2.1; No. 1193, 1.2; No. 1203, 2.3. These changes are similar to those found by Richter [1].
[f] 20-hr irradiation on each side of sheet.
[g] Change in pH during 17-hr period of irradiation.

It was found that papers having high absorption values, the newsprint and the soda-sulfite papers, deteriorated more than those having lower absorptions, such as new rag, old-rag, and refined sulfite papers. It is probable, however, that the fiber components were responsible for the differences in light stability, and that the absorption was only incidentally greater, although the two factors may have operated simultaneously. The condition of the fiber is obviously important, since the old rag papers were, in general, less stable than the new rag papers.

Other factors, such as content of lignin, rosin, and acid, are more important than the extent of absorption in determining paper deterioration, as shown strikingly by the extreme example, *N*-b, which, although having a somewhat higher absorption than *N*-a, was much more stable than the latter because of the presence of $NaHCO_3$, which apparently increased the light stability of the lignin.

Substances other than cellulose influenced the light absorption by the sheet, with varying consequences. The rosin in 1179 almost doubled the light absorption but caused little or no increase in deterioration. Certain fillers changed the absorptions of the rag papers with but slight effects on light stability. The darkening of newsprint by the addition of $NaHCO_3$ increased the absorption. These effects on light absorption arose from the presence of relatively large amounts of material. It was, therefore, of interest to change the absorption of paper by adding only minute amounts of absorbing materials. Accordingly, some experiments were conducted with papers dyed by dipping in 1-percent acetone solutions of various dyes. Aqueous solutions were avoided to preserve flatness in the sheets for adequate temperature control during irradiation.

The results in table 4 show that the dyeing doubled and trebled the light absorption but that the light stabilities of the papers were not lowered in every instance. The data indicate that certain dyes present in very small amounts are capable of transferring the absorbed radiant energy to some types of fibers in such manner as to cause deterioration. The data also show that deterioration is not proportional to the extent of absorption, other things being equal. It should be mentioned that the dyes were usually completely faded during the first half of the period of irradiation. Similar sensitization appears to have been found by others working with textile materials [15].

TABLE 4.—*Effect of various dyes*[a] *upon the light*[b] *stability of papers*

Paper number and dye	Decrease in alpha cellulose percentage	Light absorption
		Percent
1160	1.3	16
1160+eosin	4.9	32
1160+aniline yellow	1.1	47
1160+alizarin cyanine yellow	1.8	47
1160+nigrosine	2.3	
1160+sudan II	2.5	41
1214	3.4	21
1214+eosin	4.3	45
1214+cyanine green	2.4	48
1203	4.0	23
1203+eosin	3.0	47

[a] Dyed by dipping in 1-percent solutions of the dyes in acetone.
[b] 17 hours of irradiation under the usual conditions.

The absorption values given in tables 3 and 4 were calculated from reflectance and transmission values, inasmuch as the fraction of the incident light absorbed by the sheet corresponds to the light *not* lost by reflection and transmission.

The absolute total reflectance and transmission of each sheet were measured by methods described elsewhere in detail by one of the writers [14]. The reflectance at 45° from normal incidence was used. Since the carbon arc used varied greatly in color and intensity from one instant to another, average values for ½-hour periods were obtained by substituting a recording potentiometer, including a 100-ohm galvanometer, for the usual manually operated potentiometer. The light intensities necessary for the direct operation of this instrument by the photocells had to be higher than is compatible with greatest precision in the circuit used, but tests with rotating sectored disks, transmitting 25 and 50 percent, showed that transmissions could be measured to an accuracy of ±0.5-percent transmission with this arrangement.

The fractional absorption, A_p, of a sheet of paper, p, is defined in terms of its reflectance, R_p, and its transmission, T_p, as follows:

$$A_p=1-R_p-T_p. \tag{1}$$

In the case of a sheet mounted on an aluminum backing, as in the usual experimental arrangement, some of the radiant energy transmitted by the sheet is returned by reflection to the sheet. By summing up the infinite series of reflections undergone by this radiant energy between the sheet and the aluminum, it can be shown that the fraction of the total radiant energy available to the sheet by reflection from the backing of reflectance R_{Al} is $T_pR_{Al}/(1-R_pR_{Al})$, of which quantity the sheet absorbs the fraction A_p.

Combining the fractions of the incident and reflected light absorbed, it is seen that the paper mounted on the aluminum backing absorbs the fraction A'_p of the total incident light:

$$A'_p=A_p\left(1+\frac{T_pR_{Al}}{1-R_pR_{Al}}\right). \tag{2}$$

The value of R_{Al} was determined experimentally as follows: The reflectance of a paper mounted on the aluminum backing may be designated as R_{p+Al}, and can be shown by the method of summation of an infinite series to be

$$R_{p+Al}=R_p+\frac{T_p^2R_{Al}}{1-R_pR_{Al}}. \tag{3}$$

The quantities R_{p+Al}, R_p, and T_p, for the light used in the usual experimental arrangement, were measured for three thin papers, and when substituted into eq 3 gave a value of $R_{Al}=0.73$ [5] as an average of three closely agreeing results.

All the values for light absorption listed in tables 3 and 4 were calculated by using eq. 1 and 2. Since the optical values changed because of bleaching, or, in the case of newsprint, yellowing, measure-

[5] This value for the reflectance of the etched aluminum backing may be compared with 0.734, the average reflectance for the region of 400 to 740 millimicrons, obtained from a rather flat curve, using the General Electric Recording Spectrophotometer. This curve was obtained by H. J. Keegan, of the Bureau. The data were then converted to absolute values of reflectance.

ments were made before and after irradiation and the average values used for calculation.

(b) OXYGEN AND MOISTURE IN SURROUNDING ATMOSPHERE

The light stability of paper was found to be very materially increased by a lack of oxygen in the surrounding atmosphere. The data showing this for widely differing papers are given in table 5. All chemical changes during irradiation were found to be smaller in purified nitrogen than in air.

TABLE 5.—*Effect of oxygen and moisture upon the light[a] stability of papers*

Paper number	Decrease in alpha-cellulose percentage			Increase in copper-ammonia fluidity			Lowering of pH		
	Air[b]	Nitrogen[c]	Dry air[d]	Air[b]	Nitrogen[c]	Dry air[d]	Air[b]	Nitrogen[c]	Dry air[d]
WOOD-PULP PAPERS									
				Rhes	*Rhes*	*Rhes*			
1133 (soda-sulfite)	5.6	1.4	2.7	2.9	0.0	1.2	.....	.....	.....
1136 (soda-sulfite)	7.0	2.6	4.8	4.0	.1	1.2	0.4	0.2	0.55
1138 (soda-sulfite)	6.2	2.6	6.2	2.8	.3	1.4	.45	.4	.55
1166 (refined sulfite)	2.9	.....	2.5	.....	.....	.....	.....	.....	.....
N (newsprint)	31.3	6.5	20.0	9.7	5.1	.....	1.7	.75	1.6
RAG PAPERS									
1182 (new rag)	4.2	1.2	5.2	1.3	0.0	0.9	0.3	0.0	0.45
1186 (new rag)	3.0	1.4	5.3	1.7	.3	1.7	.1	.0	.35
1191 (old rag)	3.2	.3	.....	1.0	.0	.....	.4	.05	.....
1200 (old rag)	3.5	.9	5.2	1.4	.0	1.0	.85	.0	1.15
1203 (old rag)	4.0	1.0	6.8	1.4	.1	1.3	.3	.25	.8

[a] 17 hours of irradiation under the usual conditions, except as indicated.
[b] 58-percent relative humidity at 30° C.
[c] Contained less than 0.03 percent of O_2 after purification. See reference [5] for all details.
[d] Less than 0.02-percent relative humidity at 30° C.

All photochemical changes did not cease at the low concentration of oxygen, less than 0.03 percent by volume in the nitrogen used, as shown particularly by the changes in alpha cellulose. The chemical changes indicated by fluidity data, however, occurred only slightly or not at all, except in newsprint, at this concentration of oxygen. In a special experiment (described in footnote 4, page 62) with a probably much lower concentration of oxygen, the changes in newsprint were found to be practically the same as those shown in table 5. This would indicate, but, of course, not prove conclusively, that slight photochemical changes in paper occur even in the complete absence of gaseous oxygen.

The light stability of papers irradiated in extremely dry air (containing less than 0.0007 percent of gaseous water by volume) showed a fundamental difference between papers derived from wood and those derived from cotton. As seen from table 5, lack of water vapor caused smaller changes in alpha cellulose for the wood pulp papers, but larger changes for the papers derived from cotton, than resulted from light under normal conditions of moisture. The fluidity data are again inconclusive for the rag papers, as in the case of the experiments in nitrogen. It is of interest to note that the acidity of all types of papers was increased by irradiation in dry air. Control experiments in the dark showed no changes.

(c) TIME AND INTENSITY OF IRRADIATION.

The data of tables 3, 6, and 7 show that the alpha cellulose changes were proportional to less than the first power of the lengths of time of irradiation and light intensity, except, perhaps, in the early stages of irradiation. Exposure, of relatively unchanged fibers, by turning the sheet over, increased the rate of deterioration, as shown by the experiment with newsprint, *N*, table 6.

TABLE 6.—*Effect of varying the time of irradiation* [a]

Paper number	Decrease in alpha-cellulose percentage for various periods (hours) of irradiation						
	1 1/16	2 1/8	4 1/4	8 1/2	17	34	51
N (newsprint)	5.3	9.9	16.1	25.4	[b] 35.9 [a] (42.8)	.....	.....
1136 (soda-sulfite)	.....	.....	.....	3.9	7.0	10.4	12.5
1166 (refined sulfite)	.....	.....	.....	1.6	2.9	3.8	4.7
1182 (new rag)	.....	.....	.....	2.7	4.2	5.4	7.0
1203 (old rag)	.....	.....	.....	2.2	4.0	.....	8.2

[a] The usual conditions of irradiation prevailed for all the papers with the exception of one experiment with newsprint, in which case the sheet was irradiated for 8½ hours on each side. The corresponding value is given in parentheses.

[b] This value for newsprint, and that in tables 7 and 11, differ from that in tables 3, 5, and 8 because of a change of arc-lamp globes necessitated by breakage. Except for this instance, the globes were changed with sufficient frequence to avoid important differences arising from solarization of the glass.

TABLE 7.—*Effect of varying the light intensity*

Paper number	Decrease in alpha-cellulose percentage at various relative light intensities [a]					
	1.0 [b]	½	¼	⅛	1/16	1/32
N (newsprint)	35.9	29.6	23.6	15.8	8.8	4.7
1136 (soda-sulfite)	12.5	10.8	.....	.....	.....	.....
1203 (old rag)	8.2	6.7	.....	.....	.....	.....

[a] The other conditions of irradiation were as usual. The newsprint paper was irradiated for 17 hours at each intensity, and the other 2 papers were irradiated for 51 hours at each intensity.

[b] Unity represents an absolute incident intensity of 0.17 watt/cm². Variation in intensity was secured by increasing the distance between the arc and the sheet according to the inverse-square law, taking the average intensity over the sheet into account.

The departure from proportionality of alpha-cellulose change with respect to time and intensity is seen to be rather small within the first 17-hour period for the various types of papers, with the exception of newsprint. Even in the latter case the departures do not affect the conclusions based upon the various data for newsprint.

(d) LIGNIN CONTENT

The extensive deterioration by light of newsprint paper probably arises from the photochemical reactivity of lignin. Along with the large change in alpha cellulose in this paper, *N*-a of table 3, the lignin content decreased from 19.1 to 13.7 percent during irradiation.[6] The other papers contained little or no lignin; paper 1133, for example, was found to have a lignin content of less than 0.5 percent.

[6] Similar changes in lignin contents of certain types of wood during irradiation with sunlight have been observed by Richter [1].

TABLE 8.—*Effect of gaseous oxygen upon the light[a] stability of newsprint*

Composition of atmosphere[b]	Decrease in alpha-cellulose percentage	Increase[c] in copper number	Lowering of pH
Air ($21\%O_2$)	31.3	15.7	1.7
N_2[c]+1.1% O_2[d]	17.1		1.3
N_2+0.21% O_2	13.7		1.1
N_2+0.11% O_2	12.2	4.6	1.0
N_2+0.03% O_2	6.5	2.2	0.75

[a] 17 hours of irradiation under the usual conditions, excepting oxygen content.
[b] All experiments were conducted at barometric pressure.
[c] Contained argon and any other inert gases usually present in commercial "water pump" nitrogen, after purification to remove oxygen.
[d] The various oxygen pressures were obtained by evacuating the system to the desired air pressure and refilling it with purified N_2, except in the experiment with the lowest concentration of O_2, which was obtained as described in refrence [5].
[e] Copper number for the unirradiated control was 5.4.

The chemical changes in newsprint irradiated at various concentrations of oxygen are shown in table 8. The sheets yellowed according to the oxygen content; only slight yellowing occurred at the lowest oxygen content listed, and none at all in the special experiment described in footnote 4.

The light stability of newsprint is very materially increased by buffering the sheet at pH 7.2, as shown by the data for paper *N*-b, table 3. In this experiment the sheet was dipped in a solution of $NaHCO_3$, and after air-drying, it was found to have retained 0.12 g of $NaHCO_3$, which gave the sheet a pH of 7.2. During subsequent irradiation, the lignin content decreased only 2.1 percent, indicating a relationship between lignin change and cellulose deterioration.

Whatever the steps between the initial absorption of radiant energy by lignin and the change in the cellulose may be, the rate of one or more of these reactions was greatly dependent upon the acidity of the paper. Relatively large quantities of acidic substances were produced during the irradiation, as shown by the change in pH from 5.0 to 3.3 for paper *N*-a. The first cold-water extract of 1 g of sample *N*-a, after and before irradiation, was found to require 10 ml and 1 ml, respectively, of 0.01 *N* NaOH for titration to an end point of pH=7.5, using the glass electrode in the absence of CO_2. The titration curve thus obtained was characteristic of an acid much weaker than acetic, in that the voltage changes were very gradual. The pH, 3.3, at the beginning of the titration, however, corresponded to an acid stronger than acetic. These two facts together indicate that a series of acids of various degrees of ionization were formed during the irradiation. The amount of material extractable with hot water increased from 1.0 to 9.6 percent during the irradiation.

It does not seem likely, however, that the hydrogen ions which these acidic reaction products yielded were responsible for the large effect of light upon newsprint paper, inasmuch as the data of table 9 show that sulfuric acid at a pH of 3.3 had only a small effect upon the light stability of this paper.

The resinous material in newsprint apparently did not affect the light stability appeciably. It was found that a sheet which had been extracted with ethyl alcohol, benzene, and ether before irradiation showed no improvement in light stability.

The effect of moisture upon the light deterioration of highly lignified papers is seen from table 5 to be moderate from the fact that extreme desiccation had only a minor effect. At an intermediate value of relative humidity, 35 percent at 30° C, the decrease in alpha-cellulose percentage was found to be 27.9 instead of 31.3. The increase in copper number corresponding to the 17-hour period of irradiation in very dry air was 11.4.

(e) ACIDITY

The results given in table 3 show that the sulfuric acid, present in papers because of the hydrolysis of aluminum sulfate used in their manufacture, had varying effects upon light stability, depending greatly, however, upon the type of fiber. This is in contrast to the thermal stability of papers, for which the pH, irrespective of fiber content, is a most important index of stability [8a].

The decrease by acid of the light stability of papers made from new rags can be seen from the pairs 1177, 1178; 1179, 1182; 1183, 1186. On the other hand, the light stability of papers made from old rags or wood pulps was much less affected by acid, as seen from the pairs 1191, 1193; 1200, 1203; 1133, 1134; 1129, 1173; 1164, 1166. The greatly increased stability of newsprint after the addition of $NaHCO_3$ to the sheet was apparently due to an increase in the light stability of lignin in the neutral medium rather than an increase in the light stability of cellulose.

Experiments with papers containing unusually large amounts of acid gave similar results. Sheets were dipped in solutions of sulfuric acid in absolute alcohol of concentrations necessary to give a pH near 3.6 in the treated sheets, and dried before irradiation. The results given in table 9 show that acid has a much larger effect upon the light stability of the paper made from new rags, 991, than upon the others. Control sheets containing like amounts of acid showed no alpha-cellulose changes when kept in the dark for the same period used for irradiation.

TABLE 9.—*Effect of sulfuric acid* [a] *upon the light stability of papers*

Paper number	Before addition of acid		After addition of acid	
	pH	Decrease [b] in alpha-cellulose percentage	pH	Decrease [b] in alpha-cellulose percentage
WOOD-PULP PAPERS				
1133 (soda-sulfite)	6.4	5.6	3.6	6.9
N (newsprint)	5.0	[b] 9.9	3.3	12.2
1160 (refined sulfite)	6.6	1.3	3.7	3.3
RAG PAPER				
991 (new rag)	6.9	0.8	3.6	5.3

[a] Acid was added to the sheets by dipping them in solutions of sulfuric acid in absolute alcohol of the concentrations necessary to give a pH near 3.6 of the treated sheet, as determined by trial.

[b] Change during irradiation under the usual conditions for 17 hours, with the exception of the newsprint, which was irradiated for 2½ hours to secure a comparable decrease in alpha cellulose.

(f) CONTENT OF ROSIN AND OTHER SIZING MATERIALS

Rosin, in the amount and manner in which it is usually introduced into paper by flocculation with aluminum sulfate, was found to be an unimportant factor in the deterioration of paper by light, unless the acidity is injuriously high. The effect of the latter condition is exemplified by the pair 1182, 1186, table 3. The effect, furthermore, was most pronounced for new-rag papers, since the soda-sulfite paper 1138, containing much rosin, was only slightly less stable than 1129, containing no rosin. At low acidities, even for new-rag papers, relatively large amounts of rosin had little or no effect, as shown by paper 1179. Paper 1173, in spite of the rosin, was one of the more stable papers of its group.

Rosin, when added to sheets of paper by brushing with solutions of rosin in absolute alcohol, increased the deteriorating effect of light as much as or, in some instances, even more than sulfuric acid. This is shown by the results listed in table 10 for sheets thus treated with rosin before irradiation. The original light stabilities of papers made from new cotton fibers or refined wood fibers were greatly lessened by rosin thus added, whereas the stability of the ordinary wood fibers was not greatly affected.

TABLE 10.—*Effect of rosin* [a] *and "hydrogenated rosin"* [b] *upon the light stability of papers*

Paper number	Rosin	Decrease in alpha-cellulose percentage [c]	Lowering of pH [d e]
	Percent		
1134 (soda-sulfite)	0	5.3	
1134 (soda-sulfite)	3.9	7.7	
1134 (soda-sulfite)	5.9	7.5	
1160 (refined sulfite)	0	1.3	0.3
1160 (refined sulfite)	2.3	5.7	.95
1160 (refined sulfite)	4.9	6.9	1.20
1160 (refined sulfite)	10.6	7.3	1.45
991 (new rag)	0	0.8	
991 (new rag)	1.4	3.9	
991 (new rag)	3.2	4.0	
991 (new rag)	5.6	4.7	
	Hydrogenated rosin		
	Percent		
1160 (refined sulfite)	2.2	6.0	1.25
1160 (refined sulfite)	4.8	7.2	1.45
1160 (refined sulfite)	9.7	8.5	1.60

[a] Papermakers' rosin grade "F" applied to sheets from solutions in absolute alcohol.
[b] Applied to sheets from solutions in absolute alcohol. See reference [16] for information about this material.
[c] Both types of rosin were removed from sheets before alpha-cellulose determination by extraction with absolute alcohol in a Soxhlet apparatus. Control tests showed no change in the paper during extraction, and the qualitative rosin test showed practically complete extraction.
[d] pH measurements made with rosins present in the sheets.
[e] Before irradiation, the papers containing rosin had a pH near 5.4, those containing "hydrogenated rosin" had a pH near 5.6.

The pH of papers containing rosin introduced in this manner was found to be near 5.4 before irradiation. The acidity of the rosin was, therefore, not great enough to account for the deteriorative effect of light, inasmuch as the much higher acidities of sulfuric acid in the papers listed in table 9 had, in general, smaller effects.

It appeared possible that the effect of rosin might be ascribed to the presence of double bonds in the rosin acid molecules. The experiments were, therefore, repeated with a rosin the double bonds of which had presumably been eliminated by hydrogenation [16].

The results with hydrogenated rosin are also given in table 10 and show that this material decreased the light stability of the papers somewhat more, if anything, than the unsaturated rosin. The pH changes during irradiation for both types of rosin were also quite similar and resembled those of lignin in magnitude.

It appears, therefore, that properties other than the presence of double bonds or the behavior as an acid were responsible for the deteriorative effect of rosin. The remaining apparent reason, that of increased light absorption, was considered. The light absorption was measured for the sheets of paper 1160 containing 0, 2.3, 4.9, and 10.6 percent of rosin, and were found to be 16, 19, 20, and 24 percent, respectively, which values obviously do not represent sufficient increases in absorption to explain the greater deterioration, not even when the 5- to 6-percent increase in absorption due to darkening caused by irradiation of these large quantities of rosin is taken into account.

The effect of glue upon the light stability of paper appears to be small, if it existed at all, since the slight increases in deterioration of papers 991 and 1013, table 3, could easily be accounted for by the increased acidity caused by the acid in the glue sizing solution. No effect of starch was found.

The sizing materials themselves were physically and chemically affected by light. The water resistance of sized papers was found to decrease during irradiation, as was also found by Zhereboff [17] and Richter [1] for sunlight. A rosin, a glue, and a starch-sized paper were each found to have lost over half their sizing values (in terms of time of penetration of water, using the dry indicator method) during the 17-hour period of irradiation.

During irradiation the rosin in the papers of table 3 became almost completely insoluble in anhydrous ether, although its solubility in ethyl alcohol apparently remained unchanged. Its acidimetric equivalent weight, as determined by titration with alcoholic KOH decreased from 340 to 213 g per equivalent, which, together with the lowering of the pH shown in table 10, shows that the rosin is decomposed into molecules having carboxyl groups. The rosin was also found to undergo oxidation as shown by the fact that its oxidimetric equivalent weight [9c] decreased from 3.63 to 3.13 g per equivalent.

Analyses for glue and starch before and after irradiation showed decreases of 5 to 10 percent of the amount of sizing material originally present.

(g) PROTECTION BY PRINTERS' INK

The data in table 11 show that paper is extensively protected by ink against the action of light. The papers were printed at the Government Printing Office, using the regular "job black" ink. The sheets were printed on one side only, either solid black or with lowercase, 5-point-face roman type. Experiments with the latter, however, were conducted only with newsprint, inasmuch as the protection afforded by letters extends normally to but 10 to 15 percent of the area of the sheet, and was, therefore, difficult to measure accurately except for unstable papers.

TABLE 11.—*Effect of printers' ink,*[a] *solid black, in protecting papers against light*[b]

Paper number	Decrease in alpha-cellulose percentage [c]	
	Plain	Printed solid black
N	35.9	[d] 8.1 (32.5)
1129	5.1	1.4
1134	5.3	1.5
1136	7.0	0.0
1191	3.2	1.1
1216	2.5	1.8

[a] The papers were printed at the Government Printing Office, using the regular "job black" ink, through the kind cooperation of Robert H. Simmons.
[b] 17 hours of irradiation under the usual conditions.
[c] The alpha-cellulose percentage of a printed paper is appreciably lower than that of the plain paper, owing to the presence of certain alkali-soluble materials in the ink. To obtain the decrease brought about by light, therefore, the unirradiated solid-black paper was analyzed for control purposes.
[d] The value in parentheses corresponds to a paper printed in the normal way with letters. Therefore, only a small part was protected by ink.

The behavior of ink, which is principally on the surface of a sheet, is thus seen to be quite different from the behavior of a sensitizing dye. Although the ink absorbed almost all of the incident light, little or no transfer of photochemically active energy to the fibers occurred.

3. EFFECT OF LIGHT UPON SUBSEQUENT THERMAL STABILITY OF PAPERS

The increase in acidity occurring in paper during exposure to light, as shown by the fall in pH, table 3, suggests that a paper, once exposed to light, will no longer be as stable, even if stored in the dark, as the same paper had it not been so exposed. This was found to be the case.

A variety of papers were first irradiated, and then one half of each sheet was heated in an "accelerated aging" oven in the dark in air at 100° C for 72 hours, along with sheets of the same papers not previously irradiated. The irradiated papers, the irradiated and heated papers, and the heated papers were then analyzed. The alpha-cellulose changes in the third series correspond to the thermal or ordinary stabil-

TABLE 12.—*Effect of light*[a] *upon subsequent stability of papers*

Paper number	Decrease in alpha-cellulose percentage during heating [b]	
	Paper not previously irradiated	Paper previously irradiated [c]
1129	14.9	29.7
1138	5.2	13.6
1143	5.8	9.5
1166	2.8	6.1
1191	3.1	5.5
1133	0.0	2.4
1182	4.0	5.0
1200	2.0	2.3
1203	5.4	4.4

[a] 40 hours of irradiation (20 hours on each side of sheet) under the usual conditions.
[b] Heating for 72 hours at 100° C in the dark in air.
[c] These values are the result of subtracting the values for alpha-cellulose change due to light from those due to light plus heat.

ity of the papers, and are listed in column 2 of table 12. The values for alpha-cellulose decrease in the irradiated and heated papers, diminished by the values for alpha-cellulose decrease during irradiation alone, yielded the values corresponding to the thermal or ordinary stability of papers exposed to light at some time and then stored in the dark. These results are listed in column 3 of table 12, and show that most papers once irradiated may be expected to be considerably less permanent than if they had not been exposed to light.

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THERMAL EXPANSION OF SOME BRONZES

By Peter Hidnert

ABSTRACT

The results obtained in the course of independent tests and investigations on the linear thermal expansion of four groups of bronzes designated as tin-zinc, leaded, aluminum, and silicon bronzes are given for different temperature ranges. Curves showing the typical expansion and contraction characteristics of these bronzes during heating and cooling are presented. Ternary diagrams are given to show the effect of composition on the coefficients of expansion of copper-tin-zinc and copper-tin-lead alloys. In general, the coefficients of expansion of these copper-base alloys increase as the addition of tin, zinc, or lead is increased. For the range from 20° to 100° C, the average coefficients of expansion of the various bronzes were found to be between 16.8×10^{-6} and 19.0×10^{-6}/° C.

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I. INTRODUCTION

During the past 30 years, data on the linear thermal expansion of copper-base alloys designated as tin-zinc, leaded, aluminum, and silicon bronzes have been obtained at the National Bureau of Standards. These results are based on independent tests and investigations, the specific purposes of which in general were not related. Therefore, the ranges of temperature within which the bronzes were investigated differed in many cases. These data, together with some previously published results, are summarized in this paper. Ternary diagrams showing the effect of composition on the coefficients of expansion of copper-tin-zinc and copper-tin-lead alloys are given.

Available data from previous investigators on the linear thermal expansion of various bronzes of known compositions are given in table 1.[1] Some of the results in this table, in combination with data of the present paper, were used in the preparation of the ternary diagrams.

[1] Data (not listed in table 1) from 2 manufacturers have been published by N. L. Mochel, Thermal Expansion of Metals, Symposium on Effect of Temperature on the Properties of Metals, Am. Soc. Testing Materials and Am. Soc. Mech. Engrs., p. 683 (1931).

TABLE 1.—*Previously published values of coefficients of linear thermal expansion of bronzes by previous observers*

Observer	Date	Material	Chemical composition						Treatment	Average coefficients of expansion per degree centigrade					
			Cu	Sn	Zn	Pb	Ni	P		0° to 80° C	20° to 100° C	20° to 200° C	20° to 300° C	20° to 400° C	Other range
			%	%	%	%	%	%		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶
Fizeau [1]	1869	Bronze	86.3	9.7	4.0					[a]17.8					
Benoit [b] [2]	1889	Bronze	81.20	9.87	8.60	0.17				17.9					
		do	81.20	9.87	8.60	.17				18.0					
		Phosphor bronze	97.6	2.2				0.2	Hardened	17.0					
		do	97.6	2.2				.2	Annealed	17.0					
		do	94.6	4.7				.7	Hardened	17.4					
		do	94.6	4.7				.7	Annealed	17.4					
Le Chatelier [14]	1889	Bronze	90	10					do						22.0 (0° to 900° C)
		do	80	20					do						27.0 (0° to 800° C)
		do	70	30					do						29.5 (0° to 700° C)
		Aluminum bronze [c]	90						do						23.0 (0° to 900° C)
Dittenberger and Gehrcke [b] [3]	1902	Bronze	84.1	6.2	8.7	.7							[d] 18.1	[e] 18.7	[f] 19.2
Henning [g] [4]	1907	do	84	6	9										
Bein [b] [5]	1912	Bronze [k]	96	2.6	0.45								[h] 18.2	[i] 18.7	[j] 19.3
		do [l]	93.5	6.5							17.2				
Hidnert [b] [6]	1921	Phosphor bronze [m]	95.40	4.25				.37	Cast		17.5				
		do	95.40	4.25				.37	Cold-rolled		17.4	17.8	18.2		
		Chain bronze [m]	94.86	4.88				.12	Cast		17.2	17.6	18.0		
		do	94.86	4.88				.12	Cold-rolled		17.3	17.7	18.1		
		Bronze [m]	92.04	7.67				.11	Cast		17.1	17.4	17.8		
		do	92.04	7.67				.11	Cold-rolled		17.5	17.9	18.2		
		do [m]	89.69	10.14				.00	Cast		17.3	17.8	18.2		
		do	89.69	10.14				.00	Cold-rolled		17.7	18.1	18.6		
		Aluminum bronze [n]	92.17		.40		Trace		Hot-rolled		17.6	17.9	18.3		
		do [o]	92.17		.40		do		Hot-rolled and drawn.		16.5	17.3	18.2		
Hidnert [7]	1932	Bronze [o]	84.84	14.95		.21			Cast		16.6	17.2	17.8		
Wilkins [8]	1933	do [p]	85.0	5.0	5.1	4.9			do		18.0	18.2	18.6	18.8	19.3 (20° to 500° C)
		Silicon bronze [q]	94.75	0.5	1.5						17.8	18.1	18.5	18.9	19.3 (20° to 500° C)
											[r] 17.0				

Hidnert [9]	1934	Bronze	95.70	1.95		2.32		.03	Cast		17.2	17.3				
		do[a]	82.28	6.70	3.20	7.48	0.15	.05	do		18.1	[t] 18.4				
		do[a]	88.63	8.58	0.34	2.08	.25		do		17.5	17.9				
		do[a]	80.02	9.58	.60	9.45	.15	.04	do		18.4	18.6				
		do	86.75	9.97	2.75	0.53		.03	do		17.8					
		do	83.80	11.96	4.22			.02	do		17.9	18.3				
		do	87.75	12.25				.02	do		17.7	18.1				
		Leaded bronze[a]	73.00	4.45	0.25	21.79	.35	.05	do		18.9	18.8				
		do	65.40	7.75	None	26.62	.25		do		19.0	19.0				
		do	69.82	9.72		20.50		.02	do		18.6	18.8				
		do	77.00	11.08		11.90		.02	do		18.6	18.6				
		do[a]	75.86	11.57	.25	12.00	.20	.04	do		18.3	18.7				
Koiso, Kusumoto, and Yata [10]	1940	"HB-5" bronze[u]									19.1					

[a] Coefficient of expansion at 40° C.
[b] Coefficients of expansion computed from data in original publication.
[c] Aluminum, 10 percent.
[d] From 0° to 250° C.
[e] From 0° to 375° C.
[f] From 0° to 500° C.
[g] Coefficients of expansion computed from data reported by observer. Coefficient of expansion from −191° to +16° C, 15.1×10⁻⁶/° C.
[h] From 16° to 250° C.
[i] From 16° to 375° C.
[j] From 16° to 500° C.
[k] Manganese, 0.61; iron, 0.22; aluminum, 0.10 percent.
[l] Iron, 0.09 percent.
[m] Each coefficient of expansion is the average of values on 4 sections of a cast rod.
[n] Aluminum 7.34, silicon 0.09 percent.
[o] Coefficient of expansion from 20° to 600° C, 19.8×10⁻⁶/° C.
[p] Coefficients of expansion from 20° to 600° C and from 20° to 700° C, 20.0×10⁻⁶ and 20.6×10⁻⁶/° C, respectively.
[q] Silicon, 3.25 percent.
[r] From 0° to 100° C.
[s] Antimony, 0.15 percent.
[t] Second heating.
[u] Iron, 4; manganese, 4; zinc, 1 max; chromium, 0.5 max; aluminum, 10.5 percent; copper, balance.

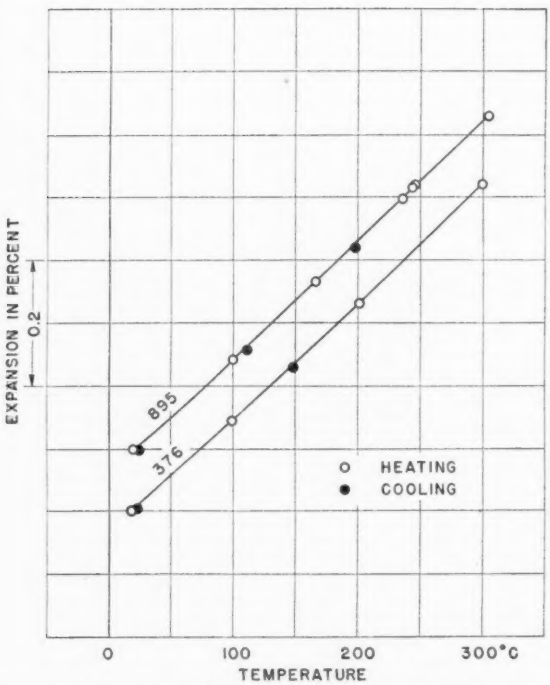

FIGURE 1.—*Linear thermal expansion of two cast tin-zinc bronzes.*

Sample 376: copper 88, tin 8, zinc 4 percent; sample 895: copper 86.5, tin 11, zinc 2.5, maximum impurities 0.2 percent.

II. MATERIALS INVESTIGATED

The samples of bronzes were provided by the American Brass Co., Waterbury, Conn., American Bronze Corporation (now American Non-Gran Bronze Corporation), Berwyn, Pa., Bridgeport Brass Co., Bridgeport, Conn., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., Fredericksen Co. (now Saginaw Bearing Co.), Saginaw, Mich., National Bureau of Standards, Titanium Alloy Mfg. Co., Niagara Falls, N. Y., and W. & L. E. Gurley, Troy, N. Y. The chemical compositions and available information regarding the treatments of the samples are given in table 2. Most of the values for chemical composition were furnished by the manufacturers.

The length of each sample used in the determinations of linear thermal expansion was 300 mm (11.8 in). The cross sections of all samples except those designated as 38 and 39 were circular, with diameters of 8 to 13 mm (0.31 to 0.51 in). The diameter in each case was the same as that of the "as received" rod. Samples 38 and 39, machined to 5 mm (0.20 in.) square section, were cut from bars having a section 16 mm (0.63 in.) square.

III. APPARATUS

The types of precision micrometric thermal-expansion apparatus used for determining the linear thermal expansion of the bronzes are described in previous publications [11, 12, 6, 13].[2] In addition to the differences in design, the instruments differed in the ranges of temperature over which they could be operated. However, essentially the same results have been obtained with each of the instruments used for the same ranges of temperature.

IV. RESULTS AND DISCUSSION

Typical expansion and contraction curves for four groups of bronzes are shown in figures 1 to 4. These figures indicate that for a relatively narrow range of temperature (fig. 1) the expansion and contraction curves nearly coincide, but in cases involving wider ranges of temperature (figs. 2 to 4) the expansion and contraction curves diverge appreciably. It is of interest to note that the expansion curves in figure 3 indicate that a marked decrease in the rate of expansion occurred in the hard-drawn aluminum bronzes at temperatures between 700° and 800° C. On the other hand, the curves for both the hard-drawn and annealed silicon bronzes (fig. 4) showed a marked increase in the rate of expansion between 900° and 1,000° C.

The average coefficients of expansion of the four groups of bronzes, computed from the expansion and contraction curves (typified by figs. 1 to 4), are given in table 2 for temperature ranges within which observations were made. The differences in length of most of the bronzes before heating and after passing through the heating and cooling cycle are also shown in this table. In general, the aluminum and silicon bronzes (figs. 3 and 4, and table 2) were investigated over wider ranges of temperature than the tin-zinc and leaded bronzes (figs. 1 and 2, and table 2).

[2] Figures in brackets indicate the literature references at the end of this paper.

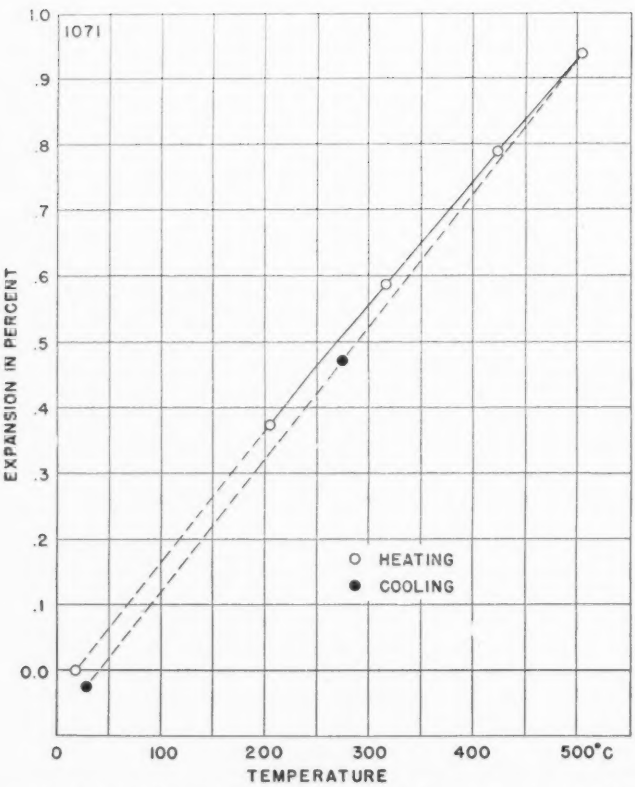

FIGURE 2.—*Linear thermal expansion of leaded bronze (treatment unknown).*

Sample 1071: copper 70, tin 9, lead 21, maximum impurities 0.2 percent.

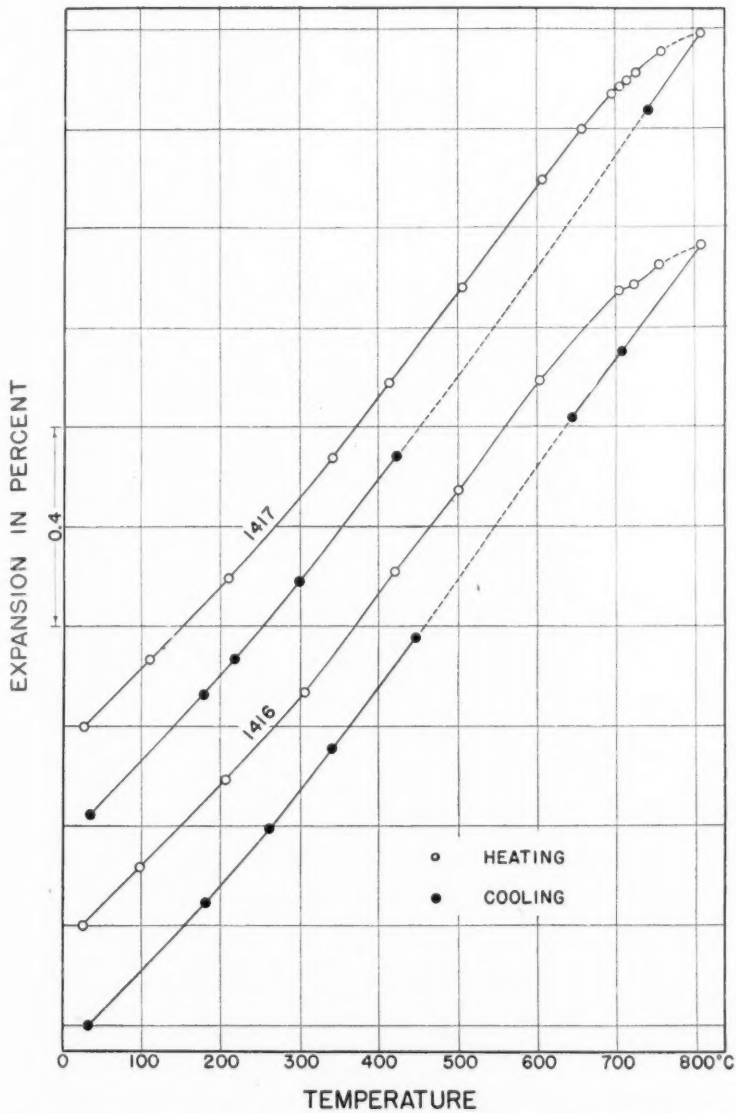

FIGURE 3.—*Linear thermal expansion of two hard-drawn aluminum bronzes.*

Sample 1416: copper 89.71, tin 0.38, aluminum 9.29, iron 0.44 percent; sample 1417: copper 89.43, tin 0.33, aluminum 9.30, iron 0.58 percent.

TABLE 2.—*Coefficients of linear expansion of four groups of bronzes*

Sample	Chemical composition									Treatment	Average coefficients of expansion (and contraction[a]) per degree centigrade											Change in length of sample after heating and cooling[b]
	Cu	Sn	Zn	Pb	Al	Si	Mn	Fe	Other elements		20° to 50° C	20° to 100° C	20° to 200° C	20° to 300° C	20° to 400° C	20° to 500° C	20° to 600° C	20° to 700° C	20° to 800° C	20° to 900° C	900° to 1000° C	
A. TIN-ZINC BRONZES																						
1105	% 98.6	% 1.3	%	%	%	%	%	% 0.02	%	Hot-rolled and annealed.	×10⁻⁶ 16.8	×10⁻⁶ 16.8	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	% −0.002
84	90	6.5	2.0	1.5						Not known	[c]17.4	[c]17.8										
308	88	10	2							Cast		17.8	18.1	18.5	18.8							−.018
376	88	8	4							do		17.8	18.1	18.5								−.004
1068	87	7	5	1						Cast at 2,250° F	[d]17.8											+.001
38	86.7	11.2	2.1							Cast and annealed at 745°C (1,373°F).	[c]17.6	[c]17.8	[c]18.0									
39											[c]17.6	[c]17.9	[c]18.1									
894	86.5	11	2.5						Maximum impurities 0.2.	Cast in green sand mold at about 2,250° F.		18.1	18.3	18.7								.000
895												17.9	18.5	18.6								−.001
B. LEADED BRONZES[a]																						
85	80	10		10						Not known		[c]18.6										
1069	76	7	4	13						Cast at 2,000° F	[f]18.4											
1071	70	9		21					Maximum impurities 0.2.	Not known			19.9	19.7 *20.1	19.5	19.3 *20.2						0.000 −.045
C. ALUMINUM BRONZES[a]																						
86	90				10.					Not known		[c]17.1										
1416	89.71	0.38	0.00		9.29			0.44	Nickel 0.18	Hard-drawn from 7/16 to 3/8 in. in diameter.		[f]16.2	16.3 *16.9	16.8 *17.7	17.9 *18.6	18.5	19.0 *19.8	18.9 *20.1	*20.3			−0.21
1417	89.43	.33	.00		9.30			.58	Nickel 0.36	Hard-drawn from 7/16 to 3/8 in. in diameter.		[f]16.2	16.4 *17.1	17.0 *17.9	18.0 *18.6	18.6	19.1	[e]19.2 *20.0	*20.4			−.19

[a] Contraction is indicated by an asterisk (*).
[b] Change in length of sample after heating and cooling is expressed as a percentage of the original length.
[c] Average of 2 values.
[d] Average of 3 values.
[e] Average of 4 values.
[f] Average of 5 values.

Sample	Chemical composition									Treatment	Average coefficients of expansion (and contraction[a]) per degree centigrade											Change in length of sample after heating and cooling[b]
	Cu	Sn	Zn	Pb	Al	Si	Mn	Fe	Other elements		20° to 50° C	20° to 100° C	20° to 200° C	20° to 300° C	20° to 400° C	20° to 500° C	20° to 600° C	20° to 700° C	20° to 800° C	20° to 900° C	900° to 1000° C	
D. SILICON BRONZES[a]																						
	%	%	%	%	%	%	%	%	%		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	%
1333	95.64	.....	0.00	.....	.....	3.04	1.03	0.09	.....	Hard drawn	.....	17.2	17.8	18.1	17.7	18.6	19.3	19.8	20.2	20.8	61.	[h]+0.57
1334	95.64	.....	.00	.....	.....	3.04	1.03	.09	.....	Annealed	.....	17.4	17.6	18.1	18.2	18.7	19.1	19.6	20.1	20.6	64.	[h]+.58
1019 [i]	94.6	.....	.00	.....	.....	4.0	1.1	.15	Phosphorus 0.06, Nickel 0.00.	Not known	17.1	17.4	.....	.....	.....	.....	.....	.....	.....	.....	.....	.00
1020											17.0	17.3	.....	.....	.....	.....	.....	.....	.....	.....	.....	.00
1021											17.1	17.4	.....	.....	.....	.....	.....	.....	.....	.....	.....	.00
1394	94.33	.....	.....	.....	.....	4.40	0.96	.11	.....	Cast	.....	17.4	17.5	18.0	18.2	18.9	19.8	20.6	21.1	21.7	.....	−.13
											.....	[e]16.3	[e]17.3	[e]17.9	.....	[e]18.8	.....	.....	[e]21.0	[e]23.1	.....	

[a] Coefficients of contraction on cooling are indicated by asterisks.

[b] Determined from the expansion curve on heating and the contraction curve on cooling. The plus sign indicates an increase in length and the minus sign a decrease in length.

[c] Determined by A. W. Gray, formerly of the National Bureau of Standards.

[d] From 20° to 40° C. Coefficients of expansion per degree centigrade from −20° to 0°, 0° to +20°, and 0° to +40° C were found to be 17.0×10⁻⁶, 17.0×10⁻⁶, and 17.4×10⁻⁶, respectively.

[e] From 20° to 150° C, determined by A. W. Gray.

[f] From 20° to 40° C. Coefficients of expansion per degree centigrade from −20° to 0°, 0° to +20°, and 0° to +40° C were found to be 17.1×10⁻⁶, 18.1×10⁻⁶, and 18.2×10⁻⁶, respectively.

[g] From 20° to 650° C.

[h] Change in length determined from length measurements on a duplicate sample before and after heating it to 1,000° C and cooling to 20° C.

[i] Chemical composition determined by G. F. Commisa, of the National Bureau of Standards.

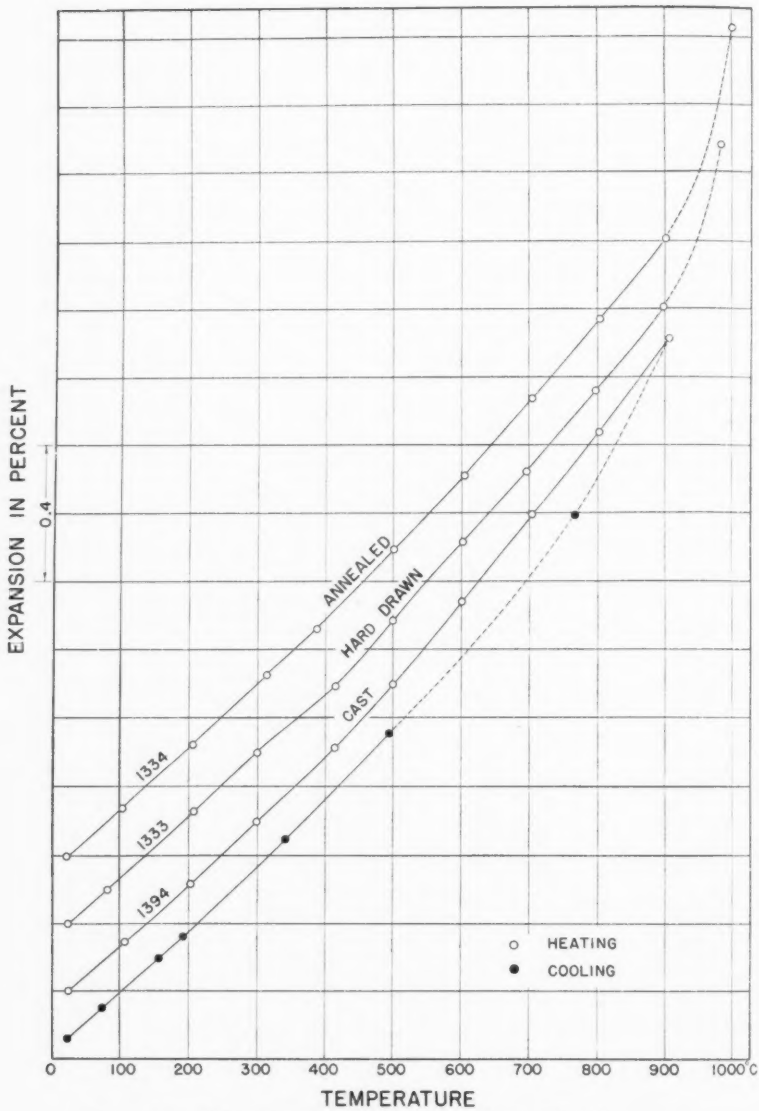

FIGURE 4.—*Linear thermal expansion of three silicon bronzes.*

Sample 1394: copper 94.33, silicon 4.40, manganese 0.96, iron 0.11 percent; samples 1333 and 1334: copper 95.64, silicon 3.04, manganese 1.03, iron 0.09 percent.

The ternary diagrams in figure 5 show the influence of additions of tin and zinc on the coefficients of expansion of copper-tin and copper-tin-zinc alloys for three ranges of temperature. The effect of different contents of tin and lead in leaded bronzes is shown in a similar manner

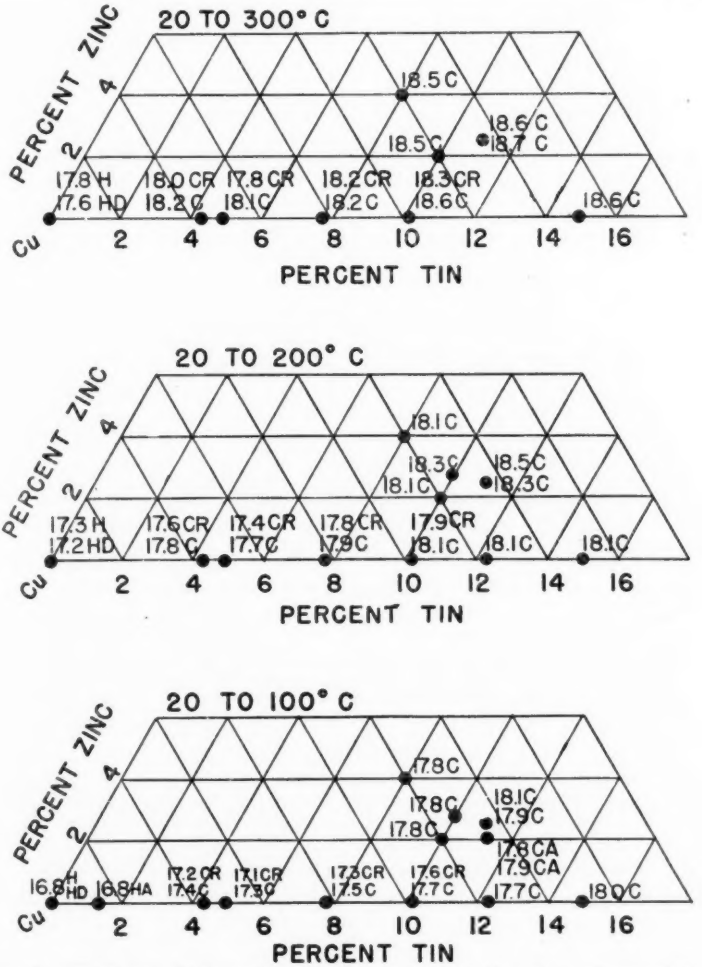

FIGURE 5.—*Portions of triangular diagrams indicating the effects of composition on the coefficints of expansion (in millionths per degree centigrade) of copper-tin and copper-tin-zinc alloys.*

C=Cast.
CA=Cast and annealed.
CR=Cold-rolled.
H=Hot-rolled.
HA=Hot-rolled and annealed.
HD=Hot-rolled and drawn.

in figures 6 and 7. These figures are based on the data in table 2 and previously published results of the author [6, 7, 9]. These diagrams show, in general, that the coefficients of expansion of the bronzes increase as the content of these addition elements is increased.

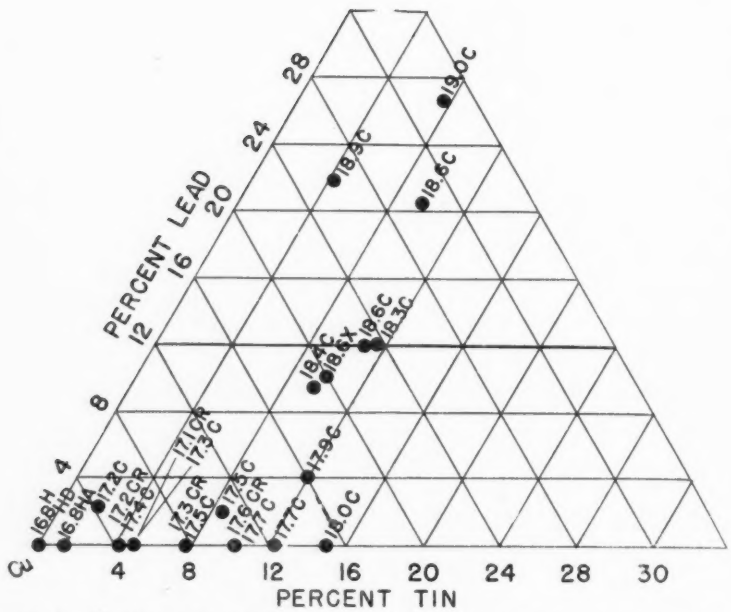

FIGURE 6.—*Portion of triangular diagram indicating the effects of composition on the coefficients of expansion (in millionths per degree centigrade) of copper-tin and copper-tin-lead alloys between 20° and 100° C.*

C=Cast.
CR=Cold-rolled.
H=Hot-rolled.
HA=Hot-rolled and annealed.
HD=Hot-rolled and drawn.
X=Treatment unknown.

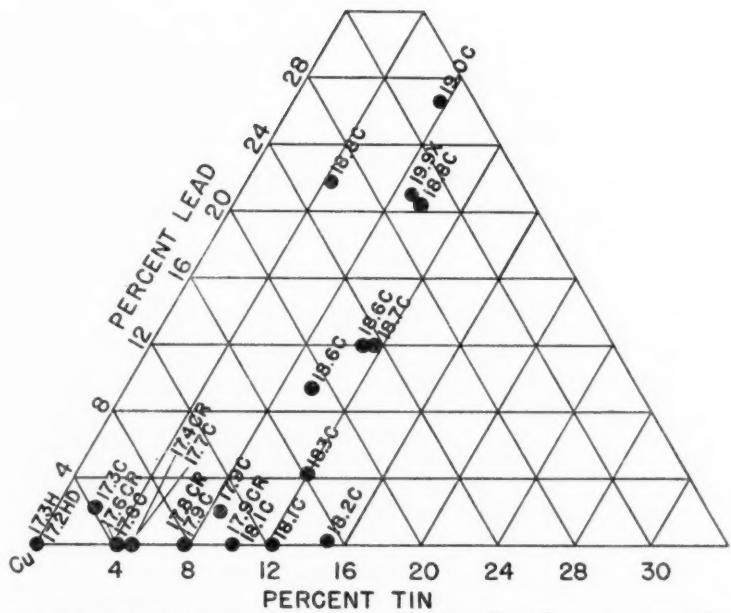

FIGURE 7.—*Portion of triangular diagram indicating the effects of composition on the coefficients of expansion (in millionths per degree centigrade) of copper-tin and copper-tin-lead alloys between 20° and 200° C.*

C=Cast.
CR=Cold-rolled.
H=Hot-rolled.
HD=Hot-rolled and drawn.
X=Treatment unknown.

The limiting coefficients of expansion of different bronzes for three temperature ranges are given in table 3.

In cases where comparison was possible, the data presented in this paper were found to be in good agreement with the results of other investigators.

TABLE 3.—*Ranges of coefficients of linear expansion* [a] *of various bronzes*

Alloys	Average coefficients of expansion per degree centigrade		
	20° to 100° C.	20° to 200° C.	20° to 300° C.
	×10⁻⁶	×10⁻⁶	×10⁻⁶
Copper-tin (0 to 15.0% tin)	16.8 to 18.0	17.2 to 18.2	17.6 to 18.6
Copper-tin-zinc (8 to 12% tin, 2 to 4% zinc)	17.8 to 18.1	18.1 to 18.5	18.5 to 18.7
Copper-tin-lead (2.0 to 11.6% tin, 2.1 to 26.6% lead)	17.2 to 19.0	17.3 to 19.9	
Copper-tin-zinc-lead (5.0 to 6.7% tin, 2 to 5.1% zinc, 1.5 to 7.5% lead).	17.8 to 18.1	18.1 to 18.4	
Copper-aluminum (7.3 to 10% aluminum)	16.2 to 17.1	16.3 to 17.3	16.8 to 18.2
Copper-silicon [b] (3.0 to 4.4% silicon)	17.2[c] to 17.4	17.5[c] to 17.8	18.0[c] to 18.1

[a] Data from previous publications by the author [6, 7, 9] were also used in the preparation of this table.
[b] Contain 1% manganese.
[c] Coefficients of contraction of a cast 4.4% silicon bronze were found to be 16.3×10⁻⁶, 17.3×10⁻⁶, and 17.9×10⁻⁶ for the ranges 100° to 20° C, 200° to 20° C, and 300° to 20° C, respectively.

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WASHINGTON, October 22, 1942.

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